

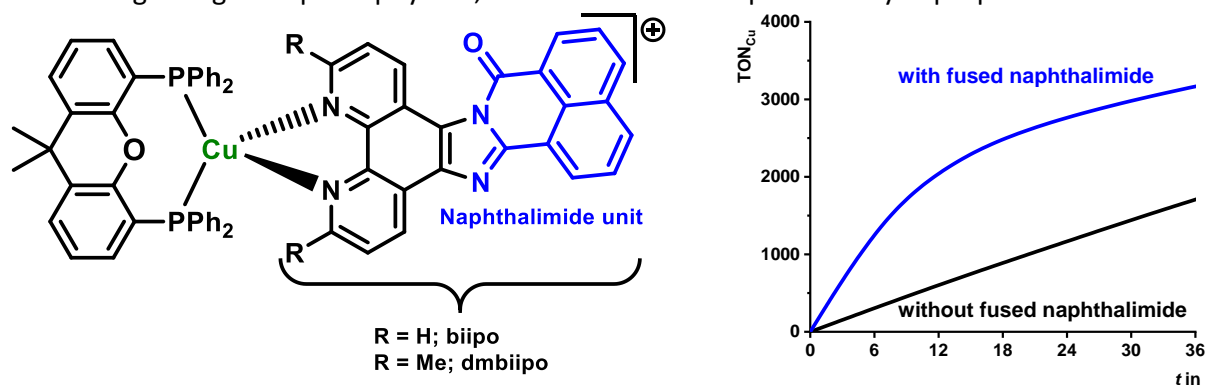
## How a fused naphthalimide unit enables advanced Cu(I) photosensitizers

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The design of novel and efficient photosensitizers that are based on earth-abundant metals are at the heart of our current research.<sup>[1-3]</sup> In this respect, we are especially focused on heteroleptic Cu(I) photosensitizers (CuPS) of the type  $[(P^{\wedge}P)Cu(N^{\wedge}N)]^+$  bearing one diphosphine ( $P^{\wedge}P$ ) and one diimine ligand ( $N^{\wedge}N$ ). It is important that these photosensitizers fulfil some basic requirements, *i.e.* a strong absorption, reversible redox processes, a high (photo)stability and a long-lived excited state.<sup>[1-3]</sup>

For this purpose, we developed a new kind of phenanthroline-based ligand with an extended  $\pi$ -system in the backbone, where a naphthalimide unit is directly fused to the phenanthroline core (biipo and dmbiipo, see figure). The resulting Cu(I) and Ru(II) complexes were extensively studied regarding their photophysical, electrochemical and photocatalytic properties.<sup>[4,5]</sup>



Left: Chemical structure of the novel Cu-based photosensitizers with the naphthalimide unit highlighted in blue. Right: Photocatalytic isomerization of *E*-Stilbene, using white light (410-730 nm) and a Cu(I)-based photosensitizer in degassed dichloromethane.

For the Cu(I) complex it was found that the MLCT excitation relaxes into a ligand-centered dark state, with a remarkably long lifetime of several microseconds in an acetonitrile solution and several hundred microseconds in the solid state.<sup>[5]</sup>

For an MLCT charge-separated excited state, the Cu(I) center would be formally oxidized to Cu(II) which prefers a different coordination environment. The so-called exciplex quenching mechanism is a major deactivation pathway for such heteroleptic Cu(I) complexes.<sup>[1]</sup> However, computational studies and time-resolved spectroscopic measurements (*i.e.* step scan FTIR) showed that the flattening in the excited state does not occur for these Cu(biipo) complexes. This lack of flattening is a strong indication for a purely ligand centered excited triplet state with a copper center in a  $d^{10}$  configuration, which may provide an enhanced catalytic activity due to the suppression of the exciplex quenching mechanism.<sup>[5]</sup>

Therefore, we tested this Cu(I) complex in the photocatalytic isomerization of *E*-stilbene. It was discovered that Cu(dmbiipo) is much more active than the related Cu(I) complex without such a naphthalimide unit or typical reference complexes like  $[Ru(bpy)_3]^{2+}$ . This illustrates, that it is not necessary for a complex to have an emissive excited state to be able to efficiently convert a substrate molecule. Instead, the excited state lifetime and the  $S_0-T_1$  energy difference are crucial factors for the photocatalytic activity.<sup>[5]</sup>

[1]: Y. Zhang, M. Schulz, M. Wächtler, M. Karnahl, B. Dietzek, *Coord. Chem. Rev.*, **2018**, 356, 127-146, DOI: 10.1016/j.ccr.2017.10.016. [2]: M. Heberle, S. Tschierlei, N. Rockstroh, M. Ringenberg, W. Frey, H. Junge, M. Beller, S. Lochbrunner, M. Karnahl, *Chem. Eur. J.*, **2017**, 23, 312-319, DOI: 10.1002/chem.201604005. [3]: M. Rentschler, M.-A. Schmid, W. Frey, S. Tschierlei, M. Karnahl, *Inorg. Chem.*, **2020**, 59, 14762-14771, DOI: 10.1021/acs.inorgchem.9b03687. [4]: Y. Yang, J. Brückmann, W. Frey, S. Rau, M. Karnahl, S. Tschierlei, *Chem. Eur. J.*, **2020**, 26, 17027-17034, DOI: 10.1002/chem.202001564. [5]: M. A. Argüello Cordero, P. Boden, M. Rentschler, P. Di Martino-Fumo, W. Frey, Y. Yang, M. Gerhards, M. Karnahl, S. Lochbrunner and S. Tschierlei, **2021**, submitted.