

## Ultrafast electronic dynamics of bridged, binuclear Ag/Au-phosphine complexes in an ion trap and in solution

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Bimetallic coinage metal complexes of type  $[M_2(dcpm)_2]^{2+}$ , ( $M = Ag, Au$ ; dcpm = bis(dicyclohexylphosphino)methane; cf. Fig. 1) exhibit unique optical and luminescence properties based on metallophilic interactions with potential applications for photocatalysis, OLED materials or sensing applications.<sup>[1,2,3]</sup> To this end it is crucial to understand the intrinsic nature of metal-metal interactions, as well as ultrafast electronic coupling dynamics and relaxation pathways in response to electronic excitation. Since studies on the ultrafast dynamics on such systems are rather scarce<sup>[3]</sup>, we investigated the excited state dynamics in parallel in gas phase by femtosecond transient photodissociation ( $\tau$ -PD)<sup>[4,5]</sup> and in solution by transient absorption (TA). Both methods reveal multiexponential decays upon excitation of the metal-centered electronic states with time constants depending on metal type, counter ions and environment (gas phase vs. solution).

Quantum chemical calculations (CC2 level of theory)<sup>[4]</sup> reveal two singlet states and corresponding triplets that display a significant shortening of the M-M distance by 0.3-0.4  relative to ground state for the  $[Ag_2(dmpm)_2]^{2+}$  (dmpm = bis(dimethylphosphino)methane) model complex.

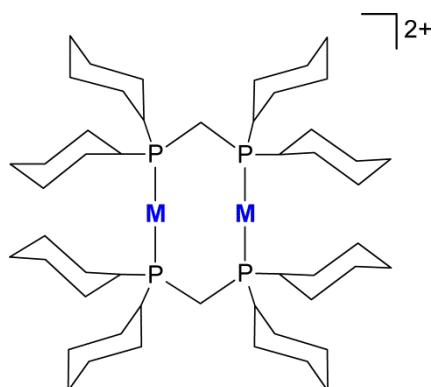


Figure 1 Schematic molecular structure of  $[M_2(dcpm)_2]^{2+}$  ( $M = Ag, Au$ ) complexes.

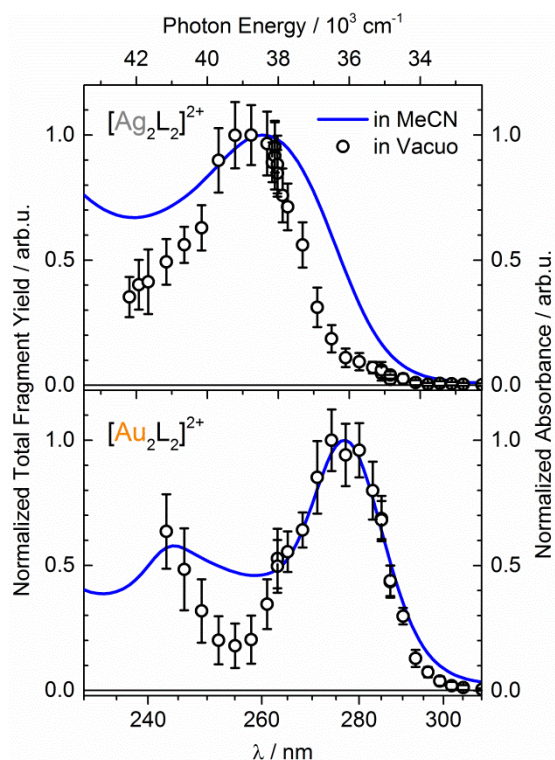


Figure 2 UV photodissociation spectra of gaseous  $[M_2(dcpm)_2]^{2+}$  species compared to absorption in MeCN ( $PF_6$  salts).

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