

# Supporting Info:DFTB3 Parametrization for Copper: the importance of orbital angular momentum dependence of Hubbard parameters

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## 1 Derivation of Orbital Angular Momentum ( $l$ ) Depen- dent Hubbard And Hubbard Derivatives for DFTB3

While for DFTB2 the  $l$ -dependent formalism has been described previously,<sup>1</sup> the third order term is derived in the following. Starting from the functional expansion, the third order term is given by:

$$E^{3\text{rd}} = \frac{1}{6} \int'' \int' \int \left[ \frac{\partial^3 E^{\text{xc}}}{\partial \rho \partial \rho' \partial \rho''} \right]_{\rho^0, \rho^{0'}, \rho^{0''}} \Delta \rho \Delta \rho' \Delta \rho'' \quad (\text{S1})$$

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Expressing the densities by superpositions of atomic and  $l$ -dependent charges and applying the same approximations as for the second order term in DFTB2 we get:

$$\begin{aligned}
E^{\Gamma'} &= \frac{1}{6} \sum_{abc} \sum_{l_a l_b l_c} \Delta q_{l_a} \Delta q_{l_b} \Delta q_{l_c} \frac{\partial \gamma_{l_a l_b}}{\partial q_{l_c}} \\
&= \frac{1}{6} \sum_{abl_a l_b} \Delta q_{l_a} \Delta q_{l_b} \left( \sum_{l'_a} \Delta q_{l'_a} \frac{\partial \gamma_{l_a l_b}}{\partial q_{l'_a}} + \sum_{l'_b (a \neq b)} \Delta q_{l'_b} \frac{\partial \gamma_{l_a l_b}}{\partial q_{l'_b}} \right)
\end{aligned} \tag{S2}$$

With symmetry of  $\gamma_{l_a l_b} = \gamma_{l_b l_a}$  and

$$\begin{aligned}
\Gamma'_{l_a l_b l'_a} &= \frac{\partial \gamma_{l_a l_b}}{\partial q_{l'_a}} = \frac{\partial \gamma_{l_a l_b}}{\partial U_{l_a}} \frac{\partial U_{l_a}}{\partial q_{l'_a}} \\
\Gamma'_{l_a l_a l'_a} &= \frac{1}{2} \frac{\partial \gamma_{l_a l_a}}{\partial q_{l'_a}} = \frac{1}{2} \frac{\partial \gamma_{l_a l_a}}{\partial U_{l_a}} \frac{\partial U_{l_a}}{\partial q_{l'_a}}.
\end{aligned} \tag{S3}$$

The third order contribution becomes

$$E^{\Gamma'} = \frac{1}{3} \sum_{ab} \sum_{l_a l_b} \Delta q_{l_a} \Delta q_{l_b} \sum_{l'_a} \Delta q_{l'_a} \Gamma'_{l_a l_b l'_a}. \tag{S4}$$

In the  $\Gamma'$ -function we now have the derivative of the  $l$ -dependent Hubbard parameter with respect to each  $l'$ -shell charge,  $l$  and  $l'$  being a shell on the same atom. To reduce the number of parameters one can make the Hubbard derivative only dependent on the atomic charge. That way the energy contribution is

$$E^{\Gamma'} \approx E^{\Gamma} = \frac{1}{3} \sum_{ab} \sum_{l_a l_b} \Delta q_{l_a} \Delta q_{l_b} \Delta q_a \Gamma_{l_a l_b}, \tag{S5}$$

where  $\Gamma_{l_a l_b}$  is given by

$$\begin{aligned}
\Gamma_{l_a l_b} &= \frac{\partial \gamma_{l_a l_b}}{\partial U_{l_a}} \frac{\partial U_{l_a}}{\partial q_a} \\
\Gamma_{l_a l_a} &= \frac{1}{2} \frac{\partial \gamma_{l_a l_a}}{\partial U_{l_a}} \frac{\partial U_{l_a}}{\partial q_a}.
\end{aligned} \tag{S6}$$

Note that through the latter approximation the results for standard DFTB3 and  $l$ -dependent

DFTB3 still are the same if the same  $l$ -dependent Hubbard and Hubbard derivative parameters for each atom type are used.

## 2 The $\gamma$ and $\Gamma$ Function at $R_{ab} = 0$

While for standard DFTB3 at zero interatomic distance  $R_{ab} = 0$  the atomic electron-electron interaction in second order is defined by the Hubbard parameter. For different atoms with different Hubbard parameters and a hypothetical interatomic distance  $R_{ab} = 0$  an interpolation formula is given in the dissertation thesis of Joachim Elsner (Joachim Elsner, dissertation thesis 1998, Universität-Gesamthochschule Paderborn, Paderborn, Germany). This interpolation formula holds also for the  $l$ -dependent  $\gamma_{l_a l'_a}$ -function and now becomes necessary in the implementation. Derivation with respect to the Hubbard gives (necessary for calculating  $\Gamma_{l_a l'_a}$ )

$$\begin{aligned} \gamma_{l_a l'_a}(r = 0, \tau_{l_a}, \tau_{l'_a}) &= \frac{1}{2} \left( \frac{\tau_{l_a} \tau_{l'_a}}{\tau_{l_a} + \tau_{l'_a}} + \frac{\tau_{l_a}^2 \tau_{l'_a}^2}{(\tau_{l_a} + \tau_{l'_a})^3} \right) \\ \frac{\partial \gamma_{l_a l'_a}(r = 0, \tau_{l_a}, \tau_{l'_a})}{\partial U_{l_a}} &= \frac{8}{5} \left( \frac{\tau_{l'_a}}{\tau_{l_a} + \tau_{l'_a}} - \frac{\tau_{l_a} \tau_{l'_a}}{(\tau_{l_a} + \tau_{l'_a})^2} + \frac{2\tau_{l_a} \tau_{l'_a}^2}{(\tau_{l_a} + \tau_{l'_a})^3} - \frac{3\tau_{l_a}^2 \tau_{l'_a}^2}{(\tau_{l_a} + \tau_{l'_a})^4} \right), \end{aligned} \quad (S7)$$

where  $l_a \neq l'_a$  and  $\tau_{l_a} = \frac{16}{5}U_{l_a}$  stands for the exponent of the spherical charge distribution (see derivation of  $\gamma$  e.g. in Joachim Elsner's thesis). Note if  $l_a = l'_a$  then  $\gamma_{l_a l_a}(r = 0, \tau_{l_a}, \tau_{l_a}) = U_{l_a}$  and the derivative becomes  $\frac{\partial \gamma_{l_a l_a}(r=0, \tau_{l_a}, \tau_{l_a})}{\partial U_{l_a}} = 1$ .

## 3 Kohn-Sham Equations

For the following derivations the notations as in the dissertation thesis of Michael Gaus are applied (Michael Gaus, dissertation thesis 2011, Karlsruhe Institute of Technology, Karlsruhe, Germany). For deriving the Kohn-Sham equations contributions of the  $l$ -dependent third order term the derivative of energy with respect to the MO coefficient is necessary.

With

$$\begin{aligned}
\Delta q_a &= q_a - q_a^0 \\
\Delta q_{l_a} &= q_{l_a} - q_{l_a}^0 \\
q_a &= \sum_i n_i \sum_{\mu \in a} \sum_b \sum_{\nu \in b} c_{\mu i} c_{\nu i} S_{\mu\nu} \\
q_{l_a} &= \sum_i n_i \sum_{\mu \in l_a} \sum_b \sum_{\nu \in b} c_{\mu i} c_{\nu i} S_{\mu\nu} \\
\frac{\partial q_a}{\partial c_{\delta i}} &= \delta_{ad} \sum_c \sum_{\nu \in c} n_i c_{\nu i} S_{\delta\nu} + \sum_{\mu \in a} n_i c_{\mu i} S_{\mu\delta} \\
\frac{\partial q_{l_a}}{\partial c_{\delta i}} &= \delta_{ad} \sum_c \sum_{\nu \in c} n_i c_{\nu i} S_{\delta\nu} + \sum_{\mu \in l_a} n_i c_{\mu i} S_{\mu\delta}
\end{aligned} \tag{S8}$$

where  $\delta_{ad} = 1$  if  $a = d$  and  $\delta_{ad} = 0$  otherwise,  $q_a$  is the Mulliken charge of atom  $a$  and  $q_{l_a}$  the Mulliken charge of the  $l$ th l-shell of atom  $a$ , and with  $\delta \in d$  ( $\delta$  is an orbital of atom  $d$ ) we get

$$\begin{aligned}
\frac{\partial E^\Gamma}{\partial c_{\delta i}} &= \frac{\partial}{\partial c_{\delta i}} \left[ \frac{1}{3} \sum_{ab} \sum_{l_a l_b} \Delta q_{l_a} \Delta q_{l_b} \Delta q_a \Gamma_{l_a l_b} \right] \\
&= \frac{1}{3} \sum_{ab} \sum_{l_a l_b} l_a l_b \frac{\partial q_{l_a}}{\partial c_{\delta i}} \Delta q_{l_b} (\Delta q_a \Gamma_{l_a l_b} + \Delta q_b \Gamma_{l_b l_a}) + \frac{1}{3} \sum_{ab} \frac{\partial q_a}{\partial c_{\delta i}} \sum_{l_a l_b} \Delta q_{l_a} \Delta q_{l_b} \Gamma_{l_a l_b} \\
&= \frac{1}{3} \sum_{ab} \sum_{l_a l_b} \sum_{\mu \in l_a} n_i c_{\mu i} S_{\mu\delta} \Delta q_{l_b} (\Delta q_a \Gamma_{l_a l_b} + \Delta q_b \Gamma_{l_b l_a}) \\
&\quad + \frac{1}{3} \sum_{bc} \sum_{l_b l_c} \sum_{\nu \in l_c} n_i c_{\nu i} S_{\delta\nu} \Delta q_{l_b} (\Delta q_d \Gamma_{l_d l_b} + \Delta q_b \Gamma_{l_b l_d}) \\
&\quad + \frac{1}{3} \sum_{ab} \sum_{\mu \in a} n_i c_{\mu i} S_{\mu\delta} \sum_{l_a l_b} \Delta q_{l_a} \Delta q_{l_b} \Gamma_{l_a l_b} + \frac{1}{3} \sum_{bc} \sum_{\nu \in c} n_i c_{\nu i} S_{\delta\nu} \sum_{l_d l_b} \Delta q_{l_d} \Delta q_{l_b} \Gamma_{l_d l_b} \\
&= \frac{1}{3} \sum_{ab} \sum_{l_a l_b} \sum_{\mu \in l_a} n_i c_{\mu i} S_{\mu\delta} \Delta q_{l_b} \left( \Delta q_a \Gamma_{l_a l_b} + \Delta q_b \Gamma_{l_b l_a} + \Delta q_d \Gamma_{l_d l_b} + \Delta q_b \Gamma_{l_b l_d} \right. \\
&\quad \left. + \sum_{l'_a} \Delta q_{l'_a} \Gamma_{l'_a l_b} + \sum_{l_d} \Delta q_{l_d} \Gamma_{l_d l_b} \right).
\end{aligned} \tag{S9}$$

During the transformations we have taken advantage of the symmetry  $S_{\mu\delta} = S_{\delta\mu}$  and have renamed indices. Dividing by  $2n_i$  and again renaming indices the Kohn-Sham equations read

$$\begin{aligned} \sum_b \sum_{l_b} \sum_{\nu \in l_b} c_{\nu i} (H_{\mu\nu} - \epsilon_i S_{\mu\nu}) &= 0 \quad \forall a, \mu \in a, \\ H_{\mu\nu} &= H_{\mu\nu}^0 + S_{\mu\nu} \sum_c \sum_{l_c} \Delta q_{l_c} \left( \frac{1}{2} (\gamma_{l_a l_c} + \gamma_{l_b l_c}) + \frac{1}{6} (\Delta q_b \Gamma_{l_b l_c} + \Delta q_c \Gamma_{l_c l_b} \right. \\ &\quad \left. + \Delta q_a \Gamma_{l_a l_c} + \Delta q_c \Gamma_{l_c l_a} + \sum_{l'_b} \Delta q_{l'_b} \Gamma_{l'_b l_c} + \sum_{l'_a} \Delta q_{l'_a} \Gamma_{l'_a l_c} \right) \end{aligned} \quad (\text{S10})$$

## 4 Total Energy

The total energy can be written as

$$\begin{aligned} E^{\text{DFTB3}} &= E^{\text{H0}} + E^\gamma + E^\Gamma + E^{\text{rep}} \\ &= \sum_{iab} \sum_{\mu \in a} \sum_{\nu \in b} n_i c_{\mu i} c_{\nu i} H_{\mu\nu}^0 + \sum_{ab} \sum_{l_a l_b} \Delta q_{l_a} \Delta q_{l_b} \left( \frac{1}{2} \gamma_{l_a l_b} + \frac{1}{3} \Delta q_a \Gamma_{l_a l_b} \right) + E^{\text{rep}} \end{aligned} \quad (\text{S11})$$

or using the eigenvalues

$$\sum_i n_i \epsilon_i = \sum_{iab} \sum_{l_a l_b} \sum_{\mu \in l_a} \sum_{\nu \in l_b} n_i c_{\mu i} c_{\nu i} H_{\mu\nu} \quad (\text{S12})$$

to get (exploiting the symmetry of  $\gamma_{ab} = \gamma_{ba}$  and the definition of  $\Delta q_a = q_a - q_a^0$ )

$$\begin{aligned}
E^{\text{DFTB3}} &= \sum_i n_i \epsilon_i - \sum_{ac} \sum_{l_a l_c} q_{l_a} \Delta q_{l_c} \left( \frac{1}{2} \gamma_{l_a l_c} + \frac{1}{3} \left( \Delta q_a \Gamma_{l_a l_c} + \Delta q_c \Gamma_{l_c l_a} + \sum_{l'_a} \Delta q_{l'_a} \Gamma_{l'_a l_c} \right) \right) \\
&\quad + \sum_{ab} \sum_{l_a l_b} \Delta q_{l_a} \Delta q_{l_b} \left( \frac{1}{2} \gamma_{l_a l_b} + \frac{1}{3} \Delta q_a \Gamma_{l_a l_b} \right) + E^{\text{rep}} \\
&= \sum_i n_i \epsilon_i - \sum_{ab} \sum_{l_a l_b} \Delta q_{l_b} \left( \frac{1}{2} (q_{l_a} + q_{l_a}^0) \gamma_{l_a l_b} + \frac{1}{3} q_{l_a}^0 \Delta q_a \Gamma_{l_a l_b} + \frac{1}{3} q_{l_a} \Delta q_b \Gamma_{l_b l_a} \right. \\
&\quad \left. + \frac{1}{3} q_{l_a} \sum_{l'_a} \Delta q_{l'_a} \Gamma_{l'_a l_b} \right) + E^{\text{rep}}
\end{aligned} \tag{S13}$$

## 5 Atomic Forces

The third order contribution to the atomic forces is given by

$$\begin{aligned}
F_{kx}^{\Gamma} &= - \frac{\partial}{\partial R_{kx}} \left[ \frac{1}{3} \sum_{ab} \sum_{l_a l_b} \Delta q_{l_a} \Delta q_{l_b} \Delta q_a \Gamma_{l_a l_b} \right] \\
&= - \frac{1}{3} \sum_{ab} \sum_{l_a l_b} \frac{\partial q_{l_a}}{\partial R_{kx}} \Delta q_{l_b} (\Delta q_a \Gamma_{l_a l_b} + \Delta q_b \Gamma_{l_b l_a}) \\
&\quad - \frac{1}{3} \sum_{ab} \sum_{l_a l_b} \Delta q_{l_a} \Delta q_{l_b} \frac{\partial q_a}{\partial R_{kx}} \Gamma_{l_a l_b} - \frac{1}{3} \sum_{ab} \sum_{l_a l_b} \Delta q_{l_a} \Delta q_{l_b} \Delta q_a \frac{\partial \Gamma_{l_a l_b}}{\partial R_{kx}} \\
&= F_{kx}^{\Gamma 1} + F_{kx}^{\Gamma 2},
\end{aligned} \tag{S14}$$

where the first and second terms are collected in  $F_{kx}^{\Gamma 1}$  and the third term is denoted  $F_{kx}^{\Gamma 2}$ .

Using

$$\begin{aligned}
\frac{\partial q_a}{\partial R_{kx}} &= \sum_{\mu \in a} \sum_{\nu \in k} \sum_i n_i c_{\mu i} c_{\nu i} \frac{\partial S_{\mu\nu}}{\partial R_{kx}} & \forall a \neq k \\
\frac{\partial q_l_a}{\partial R_{kx}} &= \sum_{\mu \in l_a} \sum_{\nu \in k} \sum_i n_i c_{\mu i} c_{\nu i} \frac{\partial S_{\mu\nu}}{\partial R_{kx}} & \forall l_a, a \neq k \\
\frac{\partial q_k}{\partial R_{kx}} &= \sum_{\mu \in k} \sum_{b \neq k} \sum_{\nu \in b} \sum_i n_i c_{\mu i} c_{\nu i} \frac{\partial S_{\mu\nu}}{\partial R_{kx}} \\
\frac{\partial q_{l_k}}{\partial R_{kx}} &= \sum_{\mu \in l_k} \sum_{b \neq k} \sum_{\nu \in b} \sum_i n_i c_{\mu i} c_{\nu i} \frac{\partial S_{\mu\nu}}{\partial R_{kx}}
\end{aligned} \tag{S15}$$

and the symmetry  $\frac{\partial S_{\mu\nu}}{\partial R_{kx}} = \frac{\partial S_{\nu\mu}}{\partial R_{kx}}$  we derive

$$\begin{aligned}
F_{kx}^{\Gamma 1} &= -\frac{1}{3} \sum_{a \neq k} \sum_b \sum_{l_a l_b} \sum_{\mu \in l_a} \sum_{\nu \in k} \sum_i n_i c_{\mu i} c_{\nu i} \frac{\partial S_{\mu\nu}}{\partial R_{kx}} \Delta q_{l_b} (\Delta q_a \Gamma_{l_a l_b} + \Delta q_b \Gamma_{l_b l_a}) \\
&\quad - \frac{1}{3} \sum_b \sum_{l_k l_b} \sum_{\mu \in l_k} \sum_{c \neq k} \sum_{\nu \in c} \sum_i n_i c_{\mu i} c_{\nu i} \frac{\partial S_{\mu\nu}}{\partial R_{kx}} \Delta q_{l_b} (\Delta q_k \Gamma_{l_k l_b} + \Delta q_b \Gamma_{l_b l_k}) \\
&\quad - \frac{1}{3} \sum_{a \neq k} \sum_b \sum_{l_a l_b} \Delta q_{l_a} \Delta q_{l_b} \Gamma_{l_a l_b} \sum_{\mu \in a} \sum_{\nu \in k} \sum_i n_i c_{\mu i} c_{\nu i} \frac{\partial S_{\mu\nu}}{\partial R_{kx}} \\
&\quad - \frac{1}{3} \sum_b \sum_{l_k l_b} \sum_{\mu \in k} \sum_{c \neq k} \sum_{\nu \in c} \sum_i n_i c_{\mu i} c_{\nu i} \frac{\partial S_{\mu\nu}}{\partial R_{kx}} \Delta q_{l_k} \Delta q_{l_b} \Gamma_{l_k l_b} \\
&= -\frac{1}{3} \sum_{a \neq k} \sum_b \sum_{l_a l_b l_k} \sum_{\mu \in l_a} \sum_{\nu \in l_k} \sum_i n_i c_{\mu i} c_{\nu i} \frac{\partial S_{\mu\nu}}{\partial R_{kx}} \Delta q_{l_b} \left( \Delta q_a \Gamma_{l_a l_b} + \Delta q_b \Gamma_{l_b l_a} \right. \\
&\quad \left. + \Delta q_k \Gamma_{l_k l_b} + \Delta q_b \Gamma_{l_b l_k} + \sum_{l'_a} \Delta q_{l'_a} \Gamma_{l'_a l_b} + \sum_{l'_k} \Delta q_{l'_k} \Gamma_{l'_k l_b} \right) \\
F_{kx}^{\Gamma 2} &= -\frac{1}{3} \sum_{b \neq k} \sum_{l_b l_k} \Delta q_{l_k} \Delta q_{l_b} \Delta q_k \frac{\partial \Gamma_{l_k l_b}}{\partial R_{kx}} - \frac{1}{3} \sum_{a \neq k} \sum_{l_a l_k} \Delta q_{l_a} \Delta q_{l_k} \Delta q_a \frac{\partial \Gamma_{l_a l_k}}{\partial R_{kx}} \\
&= -\frac{1}{3} \sum_{l_k} \Delta q_{l_k} \sum_{a \neq k} \sum_{l_a} \Delta q_{l_a} \left( \Delta q_k \frac{\partial \Gamma_{l_k l_a}}{\partial R_{kx}} + \Delta q_a \frac{\partial \Gamma_{l_a l_k}}{\partial R_{kx}} \right)
\end{aligned} \tag{S16}$$

The total force acting on one atom in one cartesian coordinate finally reads

$$\begin{aligned}
F_{kx} = & - \sum_{a \neq k} \sum_{l_a l_k} \sum_{\mu \in l_a} \sum_{\nu \in l_k} \sum_i n_i c_{\mu i} c_{\nu i} \left[ 2 \frac{\partial H_{\mu\nu}^0}{\partial R_{kx}} - 2 \epsilon_i \frac{\partial S_{\mu\nu}}{\partial R_{kx}} + \frac{\partial S_{\mu\nu}}{\partial R_{kx}} \sum_b \sum_{l_b} \left( \Delta q_{l_b} \left( \gamma_{l_a l_b} + \gamma_{l_k l_b} \right. \right. \right. \\
& \left. \left. \left. + \frac{1}{3} \left( \Delta q_a \Gamma_{l_a l_b} + \Delta q_b \Gamma_{l_b l_a} + \Delta q_k \Gamma_{l_k l_b} + \Delta q_b \Gamma_{l_b l_k} + \sum_{l'_a} \Delta q_{l'_a} \Gamma_{l'_a l_b} + \sum_{l'_k} \Delta q_{l'_k} \Gamma_{l'_k l_b} \right) \right) \right) \right] \\
& - \sum_{l_k} \Delta q_{l_k} \sum_{a \neq k} \sum_{l_a} \Delta q_{l_a} \left( \frac{\partial \gamma_{l_a l_k}}{\partial R_{kx}} + \frac{1}{3} \left( \Delta q_k \frac{\partial \Gamma_{l_k l_a}}{\partial R_{kx}} + \Delta q_a \frac{\partial \Gamma_{l_a l_k}}{\partial R_{kx}} \right) \right) - \frac{\partial E^{\text{rep}}}{\partial R_{kx}},
\end{aligned} \tag{S17}$$

where the partial derivatives of  $H_{\mu\nu}^0$  and  $S_{\mu\nu}$  are calculated numerically taking Slater-Koster tables, all other derivatives are calculated analytically (see dissertation thesis of Gaus<sup>2</sup> for additional details).

## 6 Additional data

Table S1: Parameters Defining the Repulsive Potentials

Potential energy differences in kcal/mol as calculated from B3LYP/aug-cc-pVTZ

Cu <sub>2</sub>	→	2 Cu <sup>a</sup>	42.2
CuH	→	Cu <sup>a</sup> + H <sup>a</sup>	62.9
[Cu(CO)] <sup>+</sup> + CO	→	[Cu(CO) <sub>2</sub> ] <sup>+</sup>	-37.8
[Cu(H <sub>2</sub> O)] <sup>+</sup> + H <sub>2</sub> O	→	[Cu(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup>	-41.3
[Cu(NH <sub>3</sub> )] <sup>+</sup> + NH <sub>3</sub>	→	[Cu(NH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>	-55.5
[Cu(PH <sub>3</sub> )] <sup>+</sup> + PH <sub>3</sub>	→	[Cu(PH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>	-44.1
[Cu(SH <sub>2</sub> )] <sup>+</sup> + SH <sub>2</sub>	→	[Cu(SH <sub>2</sub> ) <sub>2</sub> ] <sup>+</sup>	-40.1
Cu <sup>+</sup> + 1 CO	→	[Cu(CO)] <sup>+</sup>	-37.7
Cu <sup>+</sup> + 2 CO	→	[Cu(CO) <sub>2</sub> ] <sup>+</sup>	-75.5
Cu <sup>+</sup> + 3 CO	→	[Cu(CO) <sub>3</sub> ] <sup>+</sup>	-93.2
Cu <sup>+</sup> + 4 CO	→	[Cu(CO) <sub>4</sub> ] <sup>+</sup>	-106.5
Cu <sup>+</sup> + 1 H <sub>2</sub> O	→	[Cu(H <sub>2</sub> O)] <sup>+</sup>	-41.3
Cu <sup>+</sup> + 2 H <sub>2</sub> O	→	[Cu(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup>	-82.5
Cu <sup>+</sup> + 1 NH <sub>3</sub>	→	[Cu(NH <sub>3</sub> )] <sup>+</sup>	-59.6
Cu <sup>+</sup> + 2 NH <sub>3</sub>	→	[Cu(NH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>	-115.2
Cu <sup>+</sup> + 3 NH <sub>3</sub>	→	[Cu(NH <sub>3</sub> ) <sub>3</sub> ] <sup>+</sup>	-128.3
Cu <sup>+</sup> + 4 NH <sub>3</sub>	→	[Cu(NH <sub>3</sub> ) <sub>4</sub> ] <sup>+</sup>	-138.1
Cu <sup>+</sup> + 1 PH <sub>3</sub>	→	[Cu(PH <sub>3</sub> )] <sup>+</sup>	-56.1
Cu <sup>+</sup> + 2 PH <sub>3</sub>	→	[Cu(PH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>	-100.2
Cu <sup>+</sup> + 1 SH <sub>2</sub>	→	[Cu(SH <sub>2</sub> )] <sup>+</sup>	-46.9
Cu <sup>+</sup> + 2 SH <sub>2</sub>	→	[Cu(SH <sub>2</sub> ) <sub>2</sub> ] <sup>+</sup>	-87.0
Cu <sup>+</sup> + 3 SH <sub>2</sub>	→	[Cu(SH <sub>2</sub> ) <sub>3</sub> ] <sup>+</sup>	-100.6
Cu <sup>+</sup> + 4 SH <sub>2</sub>	→	[Cu(SH <sub>2</sub> ) <sub>4</sub> ] <sup>+</sup>	-108.4

Reference geometries for force equations as calculated from B3LYP/aug-cc-pVTZ

Cu<sub>2</sub>, Cu(CH<sub>3</sub>), Cu(CH<sub>3</sub>)<sub>2</sub><sup>-</sup>, CuH, CuOH, [Cu(H<sub>2</sub>O)]<sup>+</sup>, CuNH<sub>2</sub>, [Cu(NH<sub>3</sub>)]<sup>+</sup>, CuPH<sub>2</sub>,  
[Cu(PH<sub>3</sub>)]<sup>+</sup>, CuSH, [Cu(SH<sub>2</sub>)]<sup>+</sup>, [Cu(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>, [Cu(PH<sub>3</sub>)<sub>2</sub>]<sup>2+</sup>

Potential	Division points (a.u.)	Additional equations (a.u.)
C–Cu	3.2, 4.2, 4.8, 5.0	$V''(3.619) = 0.180$
Cu–H	2.6, 3.0, 3.6	$V''(2.801) = 0.165$
Cu–N	3.2, 4.5, 6.0, 6.4	
Cu–O	3.2, 4.2, 4.8, 5.7	
Cu–P	4.0, 5.0, 6.0, 6.8	$V''(4.205) = 0.080$
Cu–S	4.0, 5.0, 6.0, 6.8	
Cu–Cu	4.0, 4.8, 6.0, 6.4	$V''(4.303) = 0.030$

<sup>a</sup> For the calculation of  $E^{\text{at}}$  using DFTB3 the atomic spin polarization energies of  $E^{\text{spin}} = -0.00853636 \text{ E}_h$  for Cu and  $-0.04106143 \text{ E}_h$  for H are used.

Table S2: Root Mean Square Deviations (in Å) of 26 Structures in Comparison to Experimental X-ray Geometries of the Cambridge Structural Database

CSD entry <sup>a</sup>	DFTB3(+D3) <sup>b</sup>	AM1* <sup>c</sup>	PM5 <sup>d</sup>	PM6 <sup>d</sup>	B3LYP <sup>e</sup>	B97-1 <sup>e</sup>
ABETEH	1.12 (0.81)	1.34	1.54			
ABUXIE <sup>f</sup>	1.56 (1.42)	1.18	0.84	1.24		
AJEVOA	0.39 (0.38)	1.11	0.26	1.18	0.30	0.30
AJILIO	0.26 (0.23)	0.18	0.31	0.43		
AJINIQ	0.29 (0.29)	0.19	0.17	0.11	0.05	0.05
AJOROG01	0.84 (0.82)	0.73	0.86	1.17	0.89	0.87
AKEVUH	0.20 (0.26)	0.17	0.14	0.17		
ALEUCU	1.09 (1.11)	0.43	0.56	0.93		
ALIWUN	0.12 (0.13)	0.13		0.17	0.12	0.11
AMEHOP	1.07 (1.25)	0.82	0.38	0.69		
AMORCU	0.15 (0.15)	0.17	1.40	0.16	0.15	0.15
AMPRCU	0.32 (0.30)	0.55	0.55	0.37	0.30	0.29
ANCTCU <sup>f</sup>	0.93 (0.94)	0.99	0.50	1.22		
APBTCU	0.14 (0.16)	0.26	0.35	0.36		
AQCBCU	0.26 (0.30)	0.42	1.14	0.16		
ASTMEC	0.34 (0.34)	0.54	1.56	0.43	0.31	0.31
ATEVAW	0.13 (0.13)	0.20	1.78	0.31		
AVOQIL	0.46 (0.47)	0.50	0.60	0.78	0.45	0.45
AWEMAQ	0.50 (0.84)	0.67	5.65	0.70		
AYACOS	1.46 (0.49)	0.79	0.41			
CETCAM	0.33 (0.32)	0.49		0.36	0.36	0.35
DMTCCU	0.13 (0.12)	0.26	0.10	0.16	0.12	0.12
ESOXAL	0.19 (0.19)	0.18	0.20	0.26		
FEJMEN	0.61 (1.13)	0.67	6.48	0.92		
GACPOQ	0.28 (0.87)	0.32	0.34	1.71		
UKUYAA	0.66 (0.66)	0.92	0.40	0.74		
MAD	0.53 (0.53)	0.55	1.02	0.61	0.31	0.30
MAX	1.56 (1.42)	1.34	5.65	1.71	0.89	0.87

<sup>a</sup> Different from ref ? , we have excluded ATISIF and BUACUM because in the CSD coordinates of only one counter-ion instead of two are provided. Among the molecules included, copper is in the +2 oxidation state except in the following (where it is +1): ABETEH, AWEMAQ, ESOXAL, FEJMEN, UKUYAA. <sup>b</sup>

Numbers with parentheses are obtained with the D3 dispersion model parameterized for DFTB3. <sup>?</sup>

Without dispersion, geometries are optimized with the in-house DFTB code; with dispersion included, geometries are optimized with CHARMM. <sup>c</sup> Values taken from ref ? . <sup>d</sup> ABETEH and AYACOS were excluded for PM6 due to unphysical structures after geometry optimization. <sup>e</sup> Basis set is 6-31+G(d,p); due to extensive computational costs only small molecules are considered. <sup>f</sup> Hydrogen atoms have been added that are not given in the CSD.

Table S3: Maximum Number of Ligands  $n_{\max}$  for Complexes of type  $\text{Cu}^X(\text{L}_n)$  with  $n = 1, 2, \dots, n_{\max}$

Ligand	$\text{Cu}^+$	$\text{Cu}^{2+}$
CO	4	4
$\text{NH}_3$	4	6
$\text{H}_2\text{O}$	2 <sup>a</sup>	6
$\text{PH}_3$	2	2
$\text{SH}_2$	4	5
$\text{CH}_3^-$	2	2
$\text{NH}_2^-$	2	2
$\text{OH}^-$	2	4 <sup>b</sup>
$\text{PH}_2^-$	2	2
$\text{SH}^-$	3	3

<sup>a</sup> More ligands are not taken into account because quite significant geometrical differences appear already between B3LYP/aug-cc-pVTZ and PBE/6-31+G(d,p). <sup>b</sup> Only n=1,2,4 have been considered.

Table S4: Sequential Bond Dissociation Energies at 0 K excluding ZPE in kcal/mol for Cu(I) species: Deviation from B3LYP/aug-cc-pVTZ

molecule <sup>a</sup>	B3LYP <sup>b</sup>	B97-1 <sup>b</sup>	B3LYP <sup>c</sup>	PBE <sup>c</sup>	PM6	DFTB3	B3LYP <sup>b</sup> //DFTB3 <sup>d</sup>
<i>Cu(I) and neutral ligands</i>							
[Cu(CO) <sub>1</sub> ] <sup>+</sup>	37.7	-0.6	+0.6	+10.9	+28.8	+1.9	+0.6
[Cu(CO) <sub>2</sub> ] <sup>+</sup>	37.8	-0.5	+0.8	+7.7	-1.9	+4.6	+0.5
[Cu(CO) <sub>3</sub> ] <sup>+</sup>	17.7	+1.1	+0.3	+6.7	-6.2	-8.5	+0.2
[Cu(CO) <sub>4</sub> ] <sup>+</sup>	13.3	+1.3	+1.1	+7.8	-2.9	-3.7	-0.2
[Cu(NH <sub>3</sub> ) <sub>1</sub> ] <sup>+</sup>	59.6	-1.0	+3.6	+10.0	+8.7	-3.8	+0.0
[Cu(NH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>	55.5	-0.4	+2.9	+7.8	-11.6	+3.5	-0.1
[Cu(NH <sub>3</sub> ) <sub>3</sub> ] <sup>+</sup>	13.1	+1.3	+1.8	+2.8	+3.6	+0.7	-1.1
[Cu(NH <sub>3</sub> ) <sub>4</sub> ] <sup>+</sup>	9.8	+1.0	+1.5	+2.5	+3.4	+4.6	-2.1
[Cu(H <sub>2</sub> O) <sub>1</sub> ] <sup>+</sup>	41.3	-1.2	+2.9	+6.2	+6.6	+0.2	-0.0
[Cu(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup>	41.3	-1.2	+2.7	+6.2	-3.6	+3.5	-0.2
[Cu(PH <sub>3</sub> ) <sub>1</sub> ] <sup>+</sup>	56.1	-0.9	+2.0	+10.2	-69.8	-4.1	+0.2
[Cu(PH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>	44.1	+0.5	+1.6	+6.9	-121.6	+1.6	-0.1
[Cu(SH <sub>2</sub> ) <sub>1</sub> ] <sup>+</sup>	46.9	-0.6	+1.5	+9.2	— <sup>e</sup>	-2.9	-0.5
[Cu(SH <sub>2</sub> ) <sub>2</sub> ] <sup>+</sup>	40.1	+0.3	+1.6	+7.3	— <sup>e</sup>	+1.7	+0.1
[Cu(SH <sub>2</sub> ) <sub>3</sub> ] <sup>+</sup>	13.6	+1.7	+0.5	+4.2	— <sup>e</sup>	-0.5	+0.5
[Cu(SH <sub>2</sub> ) <sub>4</sub> ] <sup>+</sup>	7.8	+1.8	+1.1	+3.9	— <sup>e</sup>	+4.2	+0.1
MAD		1.0	1.7	6.9	22.4	3.1	0.4
MAX		1.8	3.6	10.9	121.6	8.5	2.1
<i>Cu(I) and charged ligands</i>							
[Cu(CH <sub>3</sub> ) <sub>1</sub> ]	235.2	-2.2	+5.0	+15.8	+15.0	-10.8	+2.1
[Cu(CH <sub>3</sub> ) <sub>2</sub> ] <sup>-</sup>	74.1	+2.1	+2.0	+5.9	-34.5	-14.9	+1.9
[Cu(NH <sub>2</sub> ) <sub>1</sub> ]	223.4	-1.9	+5.6	+16.3	+17.6	+9.3	+1.3
[Cu(NH <sub>2</sub> ) <sub>2</sub> ] <sup>-</sup>	82.0	+1.0	+3.3	+6.4	-19.7	-6.8	-0.4
[Cu(OH) <sub>1</sub> ]	211.6	-1.7	+4.5	+14.3	+6.0	+16.8	-0.1
[Cu(OH) <sub>2</sub> ] <sup>-</sup>	83.8	+0.5	+3.1	+5.9	-12.2	-3.5	-0.6
[Cu(PH <sub>2</sub> ) <sub>1</sub> ]	207.2	-2.3	+3.6	+14.7	-62.2	-4.6	+1.1
[Cu(PH <sub>2</sub> ) <sub>2</sub> ] <sup>-</sup>	62.7	+2.4	+1.0	+5.8	-135.4	-9.9	+1.0
[Cu(SH) <sub>1</sub> ]	194.6	-1.6	+2.3	+12.9	— <sup>e</sup>	+3.2	-0.2
[Cu(SH) <sub>2</sub> ] <sup>-</sup>	68.0	+1.7	+0.7	+5.3	— <sup>e</sup>	-8.4	+0.0
[Cu(SH) <sub>3</sub> ] <sup>2-</sup>	-59.6	+2.2	-0.2	+1.5	— <sup>e</sup>	-7.9	-1.4
MAD		1.8	2.8	9.5	37.8	8.7	0.9
MAX		2.4	5.6	16.3	135.4	16.7	2.1

<sup>a</sup> The non-dissociated molecule is listed. <sup>b</sup> basis set aug-cc-pVTZ <sup>c</sup> basis set 6-31+G(d,p) <sup>d</sup> B3LYP single point calculations on top of DFTB3 geometries. <sup>e</sup> Because of large geometrical errors for the Cu-S bonds at the PM6 level of theory the respective complexes are excluded from the statistics.

Table S5: Sequential Bond Dissociation Energies at 0 K excluding ZPE in kcal/mol for Cu(II) species: Deviation from B3LYP/aug-cc-pVTZ

molecule <sup>a</sup>	B3LYP <sup>b</sup>	B97-1 <sup>b</sup>	B3LYP <sup>c</sup>	PBE <sup>c</sup>	PM6	DFTB3	B3LYP <sup>b</sup> //DFTB3 <sup>d</sup>
<i>Cu(II) and neutral ligands</i>							
[Cu(CO) <sub>1</sub> ] <sup>2+</sup>	93.8	-1.5	-0.2	+15.5	+25.6	+9.7	+0.4
[Cu(CO) <sub>2</sub> ] <sup>2+</sup>	68.0	-0.7	-0.3	+4.6	-6.5	+3.8	+0.3
[Cu(CO) <sub>3</sub> ] <sup>2+</sup>	43.8	+0.2	+0.6	+9.5	+5.3	+0.2	+0.4
[Cu(CO) <sub>4</sub> ] <sup>2+</sup>	32.3	+1.3	+0.8	+6.4	-4.0	-3.0	+0.5
[Cu(NH <sub>3</sub> ) <sub>1</sub> ] <sup>2+</sup>	155.9	-2.0	+3.5	+18.3	-16.4	-15.1	-0.3
[Cu(NH <sub>3</sub> ) <sub>2</sub> ] <sup>2+</sup>	103.6	-0.4	+2.1	+4.4	-17.5	-1.4	+0.2
[Cu(NH <sub>3</sub> ) <sub>3</sub> ] <sup>2+</sup>	64.7	+0.4	+3.1	+8.2	-4.3	-3.2	+0.0
[Cu(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup>	42.5	+1.4	+2.5	+4.7	-2.5	-0.8	-0.5
[Cu(H <sub>2</sub> O) <sub>1</sub> ] <sup>2+</sup>	117.4	-2.5	+3.5	+20.2	-20.0	+0.2	+0.2
[Cu(H <sub>2</sub> O) <sub>2</sub> ] <sup>2+</sup>	86.4	-1.5	+2.4	+6.0	-18.6	+4.9	+0.3
[Cu(H <sub>2</sub> O) <sub>3</sub> ] <sup>2+</sup>	61.4	+0.5	+1.0	-3.4	-2.1	-6.2	-0.4
[Cu(H <sub>2</sub> O) <sub>4</sub> ] <sup>2+</sup>	42.9	+0.7	+2.4	+2.1	+1.3	-1.7	-0.5
[Cu(PH <sub>3</sub> ) <sub>1</sub> ] <sup>2+</sup>	168.3	-3.6	+2.5	+19.3	-101.5	-10.7	-0.4
[Cu(PH <sub>3</sub> ) <sub>2</sub> ] <sup>2+</sup>	79.1	+0.4	+1.8	+5.8	-99.8	+3.6	+1.0
[Cu(SH <sub>2</sub> ) <sub>1</sub> ] <sup>2+</sup>	149.2	-3.2	+2.3	+20.7	— <sup>f</sup>	-11.4	-0.1
[Cu(SH <sub>2</sub> ) <sub>2</sub> ] <sup>2+</sup>	76.9	-0.1	+1.6	+9.0	— <sup>f</sup>	+2.7	-4.1
[Cu(SH <sub>2</sub> ) <sub>3</sub> ] <sup>2+</sup>	50.5	+1.4	+0.7	+4.7	— <sup>f</sup>	-1.9	+1.5
[Cu(SH <sub>2</sub> ) <sub>4</sub> ] <sup>2+</sup>	28.6	+2.5	+1.2	+4.3	— <sup>f</sup>	+3.8	+0.3
MAD		1.4	1.8	9.3	23.2	4.7	0.6
MAX		3.6	3.5	20.7	101.5	15.1	4.1
<i>Cu(II) and charged ligands</i>							
[Cu(CH <sub>3</sub> ) <sub>1</sub> ] <sup>+</sup>	514.4	-4.2	+5.1	+21.6	-23.9	-28.7	+0.0
[Cu(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>	223.6	+0.9	+3.6	+11.4	-11.5	-7.3	+3.2
[Cu(NH <sub>2</sub> ) <sub>1</sub> ] <sup>+</sup>	518.5	-4.2	+7.2	+23.4	-12.3	-17.8	-0.5
[Cu(NH <sub>2</sub> ) <sub>2</sub> ] <sup>+</sup>	228.5	+0.2	+4.0	+13.8	-35.2	+16.7	+2.5
[Cu(OH) <sub>1</sub> ] <sup>+</sup>	476.2	-3.3	+5.3	+23.5	-33.9	+5.9	-0.6
[Cu(OH) <sub>2</sub> ] <sup>+</sup>	239.0	-0.2	+3.5	+11.0	-39.5	+18.5	+0.4
[Cu(PH <sub>2</sub> ) <sub>1</sub> ] <sup>+</sup>	497.6	-5.2	+4.3	+21.2	-99.6	-29.3	+0.2
[Cu(PH <sub>2</sub> ) <sub>2</sub> ] <sup>+</sup>	188.4	+0.6	+2.3	+12.1	-116.7	+3.2	+2.1
[Cu(SH) <sub>1</sub> ] <sup>+</sup>	472.7	-4.9	+2.9	+22.2	— <sup>f</sup>	-14.9	-0.7
[Cu(SH) <sub>2</sub> ] <sup>+</sup>	195.2	+1.0	+1.6	+11.9	— <sup>f</sup>	+6.8	+0.2
[Cu(SH) <sub>3</sub> ] <sup>-</sup>	48.2	—	+0.5	+1.7	— <sup>f</sup>	+4.9	-0.4
MAD		2.5	3.7	15.8	46.6	14.0	1.0
MAX		5.2	7.2	23.5	116.7	29.3	3.2

<sup>a</sup> The non-dissociated molecule is listed. <sup>b</sup> basis set aug-cc-pVTZ <sup>c</sup> basis set 6-31+G(d,p) <sup>d</sup> B3LYP single point calculations on top of DFTB3 geometries. <sup>e</sup> Structure optimizes to a tetraetric conformation in contrast to a nearly planar one as B3LYP results show. <sup>f</sup> Because of large geometrical errors for the Cu-S bonds at the PM6 level of theory the respective complexes are excluded from the statistics.

Table S6: Gas Phase Proton Affinities at 0 K excluding ZPE in kcal/mol: Deviation from B3LYP/aug-cc-pVTZ

molecule <sup>a</sup>	B3LYP <sup>b</sup>	B97-1 <sup>b</sup>	B3LYP <sup>c</sup>	PBE <sup>c</sup>	PM6 <sup>d</sup>	DFTB3 <sup>e</sup>	B3LYP <sup>b</sup> //DFTB3 <sup>f</sup>
<i>Cu(I)</i>							
[Cu(NH <sub>3</sub> ) <sub>1</sub> ] <sup>+</sup>	247.1	+3.1	-0.2	-6.9	-8.0	-9.0	-0.1
[Cu(NH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>	269.1	+2.2	+0.6	-4.0	-2.0	-3.7	+0.2
[Cu(H <sub>2</sub> O) <sub>1</sub> ] <sup>+</sup>	224.9	+3.5	-1.1	-9.4	-7.9	-11.7	-0.3
[Cu(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup>	240.9	+2.5	-0.4	-6.9	-4.7	-6.3	-0.3
[Cu(PH <sub>3</sub> ) <sub>1</sub> ] <sup>+</sup>	220.8	+2.1	-1.6	-7.0	+0.4	-7.1	+0.0
[Cu(PH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>	242.7	+0.8	-0.1	-5.5	+9.4	-4.7	+0.5
[Cu(SH <sub>2</sub> ) <sub>1</sub> ] <sup>+</sup>	207.0	+1.9	-2.5	-6.4	— <sup>g</sup>	-4.6	-0.8
[Cu(SH <sub>2</sub> ) <sub>2</sub> ] <sup>+</sup>	222.7	+1.0	-1.3	-4.7	— <sup>g</sup>	+0.6	-0.6
MAD		2.1	1.0	6.4	5.4	6.0	0.4
MAX		3.5	2.5	9.4	9.4	11.7	0.8
<i>Cu(II)</i>							
[Cu(NH <sub>3</sub> ) <sub>1</sub> ] <sup>2+</sup>	48.3	+4.5	-1.9	-5.8	-3.2	+6.7	+1.4
[Cu(NH <sub>3</sub> ) <sub>2</sub> ] <sup>2+</sup>	92.6	+4.5	-2.4	-9.3	-5.6	+2.8	+1.0
[Cu(H <sub>2</sub> O) <sub>1</sub> ] <sup>2+</sup>	36.4	+3.8	-1.3	-4.7	+5.4	-0.7	+0.5
[Cu(H <sub>2</sub> O) <sub>2</sub> ] <sup>2+</sup>	73.0	+3.2	-1.6	-4.7	+1.5	-0.5	+0.1
[Cu(PH <sub>3</sub> ) <sub>1</sub> ] <sup>2+</sup>	42.7	+2.2	-1.9	-4.4	+6.0	+10.9	+0.3
[Cu(PH <sub>3</sub> ) <sub>2</sub> ] <sup>2+</sup>	76.1	+2.3	-1.8	-5.4	+27.7	+15.3	+1.4
[Cu(SH <sub>2</sub> ) <sub>1</sub> ] <sup>2+</sup>	31.1	+2.7	-2.2	-4.0	— <sup>g</sup>	+5.1	+0.3
[Cu(SH <sub>2</sub> ) <sub>2</sub> ] <sup>2+</sup>	67.1	+2.2	-2.1	-1.6	— <sup>g</sup>	+6.8	-3.6
[Cu(SH <sub>2</sub> ) <sub>3</sub> ] <sup>2+</sup>	97.6	+1.4	-2.3	-3.0	— <sup>g</sup>	+2.4	-1.9
MAD		3.0	1.9	4.8	8.2	5.7	1.2
MAX		4.5	2.4	9.3	27.7	15.3	3.6

<sup>a</sup> The protonated form is listed. <sup>b</sup> aug-cc-pVTZ <sup>c</sup> 6-31+G(d,p) <sup>d</sup> The energy of the proton in PM6 is in error by -54 kcal/mol which has been corrected for the given proton affinities. See discussion at [http://openmopac.net/manual/pm6\\_accuracy.html](http://openmopac.net/manual/pm6_accuracy.html). <sup>e</sup> NHmod parameters used, for details see ref ? . <sup>f</sup> B3LYP single point calculations on top of DFTB3 geometries. <sup>g</sup> Because of large geometrical errors for the Cu-S bonds at the PM6 level of theory the respective complexes are excluded from the statistics.

Table S7: Bond Dissociation Energies for one Ligand at 0 K excluding ZPE in kcal/mol: Deviation from B3LYP/aug-cc-pVTZ for the Mixed Ligand Test Set

Non-Dissociated System <sup>a</sup>	B3LYP <sup>b</sup>	B97-1 <sup>b</sup>	B3LYP <sup>c</sup>	PBE <sup>c</sup>	DFTB3	B3LYP <sup>b</sup> //DFTB3 <sup>d</sup>
Cu[(OH)(NH <sub>3</sub> ) <sub>4</sub> ] <sup>+</sup>	12.6	+1.4	+1.7	+2.8	+1.3	-0.7
Cu[(SH)(NH <sub>3</sub> ) <sub>4</sub> ] <sup>+</sup>	10.4	+2.0	+1.5	+3.0	+3.0	-1.6
Cu[(H <sub>2</sub> O) <sub>2</sub> (NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup>	15.1	+1.1	+1.9	+3.2	+4.6	-1.0
Cu[(SH <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O)(NH <sub>3</sub> ) <sub>2</sub> ] <sup>2+</sup>	33.9	+1.5	+2.5	+3.4	-0.2	+1.0
Cu[(SH <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ] <sup>2+</sup>	14.3	+1.4	+2.4	+2.9	+5.8	+0.5
Cu[(SH <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ] <sup>2+</sup>	22.6	+1.2	+2.2	+2.2	+2.5	-0.2
Cu[(SH <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ] <sup>2+</sup>	15.2	+1.3	+2.5	+1.5	+4.6	+1.5
Cu[(SH <sub>2</sub> ) <sub>3</sub> (NH <sub>3</sub> ) <sub>2</sub> ] <sup>2+</sup>	15.2	+1.7	+1.3	+3.6	+4.1	-0.4
Cu[(SH <sub>2</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sup>2+</sup>	13.1	+1.4	+2.4	+2.4	+7.3	+0.6
MAD		1.4	2.0	2.8	3.7	0.8
MAX		2.0	2.5	3.6	7.3	1.6

<sup>a</sup> BDE for one ligand marked with a \*. <sup>b</sup> aug-cc-pVTZ <sup>c</sup> 6-31+G(d,p) <sup>d</sup> B3LYP single point calculations on top of DFTB3 geometries.

Table S8: Relative Energy for Molecules of the Large Molecules Test Set

relative energy <sup>a</sup> in comparison to	DFTB3//DFTB3 DFTB3//B3LYP	B3LYP//B3LYP B3LYP//DFTB3
<i>Cu(I)</i>		
[Cu(-O-CH <sub>3</sub> ) <sub>1</sub> ]	-1.4	-1.0
[Cu(-O-CH <sub>3</sub> ) <sub>2</sub> ] <sup>-</sup>	-3.5	-2.6
[Cu(-S-CH <sub>3</sub> ) <sub>1</sub> ]	-0.2	-0.2
[Cu(-S-CH <sub>3</sub> ) <sub>2</sub> ] <sup>-</sup>	-0.4	-0.4
[Cu(-S-CH <sub>3</sub> ) <sub>3</sub> ] <sup>2-</sup>	-0.6	-0.6
[Cu(HS-CH <sub>3</sub> ) <sub>1</sub> ] <sup>+</sup>	-0.4	-0.5
[Cu(HS-CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>	-0.6	-0.7
[Cu(HS-CH <sub>3</sub> ) <sub>3</sub> ] <sup>+</sup>	-1.1	-1.2
[Cu(HS-CH <sub>3</sub> ) <sub>4</sub> ] <sup>+</sup>	-1.5	-1.8
[Cu(N(=CH <sub>2</sub> )(CH <sub>3</sub> ) <sub>1</sub> ) <sup>+</sup>	-1.0	-0.9
[Cu(N(=CH <sub>2</sub> )(CH <sub>3</sub> ) <sub>2</sub> ) <sup>+</sup>	-1.6	-1.5
[Cu(N(=CH <sub>2</sub> )(CH <sub>3</sub> ) <sub>3</sub> ) <sup>+</sup>	-4.2	-3.7
[Cu(N(=CH <sub>2</sub> )(CH <sub>3</sub> ) <sub>4</sub> ) <sup>+</sup>	-5.9	-5.1
[Cu(S(CH <sub>3</sub> ) <sub>2</sub> ) <sub>1</sub> ] <sup>+</sup>	-0.3	-0.4
[Cu(S(CH <sub>3</sub> ) <sub>2</sub> ) <sub>2</sub> ] <sup>+</sup>	-0.8	-0.8
[Cu(S(CH <sub>3</sub> ) <sub>2</sub> ) <sub>3</sub> ] <sup>+</sup>	-2.1	-2.1
[Cu(S(CH <sub>3</sub> ) <sub>2</sub> ) <sub>4</sub> ] <sup>+</sup>	-4.1	-2.6
[Cu(C <sub>3</sub> N <sub>2</sub> H <sub>3</sub> ) <sub>1</sub> ] <sup>b</sup>	-1.1	-1.0
[Cu(C <sub>3</sub> N <sub>2</sub> H <sub>3</sub> ) <sub>2</sub> ] <sup>- b</sup>	-2.0	-1.8
[Cu(O=CH <sub>2</sub> ) <sub>1</sub> ] <sup>+</sup>	-1.7	-1.3
[Cu(O=CH <sub>2</sub> ) <sub>2</sub> ] <sup>+</sup>	-3.1	-2.3
[Cu(imidazole) <sub>1</sub> ] <sup>+</sup>	-1.4	-1.1
[Cu(imidazole) <sub>2</sub> ] <sup>+</sup>	-2.4	-2.0
[Cu(imidazole) <sub>3</sub> ] <sup>+</sup>	-4.5	-5.3
[Cu(imidazole) <sub>4</sub> ] <sup>+</sup>	-6.5	-5.1
Cu(-S-CH <sub>3</sub> )(N(=CH <sub>2</sub> )(CH <sub>3</sub> ))	-1.3	-1.3
[Cu(-S-CH <sub>3</sub> )(C <sub>3</sub> N <sub>2</sub> H <sub>3</sub> )] <sup>- b</sup>	-1.4	-1.3
Cu(-S-CH <sub>3</sub> )(imidazole)	-1.8	-1.5
[Cu(-S-CH <sub>3</sub> )(HS-CH <sub>3</sub> ) <sub>1</sub> ]	-0.8	-0.7
[Cu(-S-CH <sub>3</sub> )(HS-CH <sub>3</sub> ) <sub>2</sub> ]	-5.0	-2.5
[Cu(C <sub>3</sub> N <sub>2</sub> H <sub>3</sub> )(imidazole) <sub>1</sub> ] <sup>b</sup>	-2.1	-1.9
[Cu(C <sub>3</sub> N <sub>2</sub> H <sub>3</sub> )(imidazole) <sub>3</sub> ] <sup>b</sup>	-7.6	-8.2
MAD	2.3	2.0
MAX	7.6	8.2
<i>Cu(II)</i>		
[Cu(-O-CH <sub>3</sub> ) <sub>1</sub> ] <sup>+</sup>	-2.6	-1.8
[Cu(-O-CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>	-3.9	-2.6
[Cu(-S-CH <sub>3</sub> ) <sub>1</sub> ] <sup>+</sup>	-0.5	-0.4
[Cu(-S-CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>	-0.2	-0.2
[Cu(-S-CH <sub>3</sub> ) <sub>3</sub> ] <sup>-</sup>	-0.5	-0.7
[Cu(HS-CH <sub>3</sub> ) <sub>1</sub> ] <sup>2+</sup>	-2.2	-1.4
[Cu(HS-CH <sub>3</sub> ) <sub>2</sub> ] <sup>2+</sup>	-1.0	-1.1
[Cu(HS-CH <sub>3</sub> ) <sub>3</sub> ] <sup>2+</sup>	-1.9	-2.6
[Cu(HS-CH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup>	-1.6	-1.7
[Cu(N(=CH <sub>2</sub> )(CH <sub>3</sub> ) <sub>1</sub> ) <sup>2+</sup>	-0.9	-0.8
[Cu(N(=CH <sub>2</sub> )(CH <sub>3</sub> ) <sub>2</sub> ) <sup>2+</sup>	-3.7	-3.5
[Cu(N(=CH <sub>2</sub> )(CH <sub>3</sub> ) <sub>3</sub> ) <sup>2+</sup>	-1.9	-2.0
[Cu(N(=CH <sub>2</sub> )(CH <sub>3</sub> ) <sub>4</sub> ) <sup>2+</sup>	-2.5	-2.6
[Cu(S(CH <sub>3</sub> ) <sub>2</sub> ) <sub>1</sub> ] <sup>2+</sup>	-2.4	-3.3
[Cu(S(CH <sub>3</sub> ) <sub>2</sub> ) <sub>2</sub> ] <sup>2+</sup>	-1.7	-1.6
[Cu(S(CH <sub>3</sub> ) <sub>2</sub> ) <sub>3</sub> ] <sup>2+</sup>	-1.6	-1.7
[Cu(S(CH <sub>3</sub> ) <sub>2</sub> ) <sub>4</sub> ] <sup>2+</sup>	-1.7	-1.9
[Cu(C <sub>3</sub> N <sub>2</sub> H <sub>3</sub> ) <sub>1</sub> ] <sup>+</sup> <sup>b</sup>	-1.9	-1.8
[Cu(C <sub>3</sub> N <sub>2</sub> H <sub>3</sub> ) <sub>2</sub> ] <sup>b</sup>	-2.8	-2.5
[Cu(O=CH <sub>2</sub> ) <sub>1</sub> ] <sup>2+</sup>	-0.9	-0.7
[Cu(O=CH <sub>2</sub> ) <sub>2</sub> ] <sup>2+</sup>	-1.4	-1.6
[Cu(imidazole) <sub>1</sub> ] <sup>2+</sup>	-2.7	-2.3
[Cu(imidazole) <sub>2</sub> ] <sup>2+</sup>	-2.3	-1.9
[Cu(imidazole) <sub>3</sub> ] <sup>2+</sup>	-3.7	-3.2
[Cu(-S-CH <sub>3</sub> )(N(=CH <sub>2</sub> )(CH <sub>3</sub> ))] <sup>+</sup>	-0.9	-1.1
Cu(-S-CH <sub>3</sub> )(C <sub>3</sub> N <sub>2</sub> H <sub>3</sub> ) <sup>b</sup>	-1.3	-1.1
[Cu(-S-CH <sub>3</sub> )(imidazole)] <sup>+</sup>	-1.4	-1.2
[Cu(-S-CH <sub>3</sub> )(HS-CH <sub>3</sub> ) <sub>1</sub> ] <sup>+</sup>	-0.7	-0.7
[Cu(-S-CH <sub>3</sub> )(HS-CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>	-2.0	-1.7
[Cu(-S-CH <sub>3</sub> )(HS-CH <sub>3</sub> ) <sub>3</sub> ] <sup>+</sup>	-2.5	-2.7
[Cu(C <sub>3</sub> N <sub>2</sub> H <sub>3</sub> )(imidazole) <sub>1</sub> ] <sup>+</sup> <sup>b</sup>	-3.7	-3.7
[Cu(C <sub>3</sub> N <sub>2</sub> H <sub>3</sub> )(imidazole) <sub>2</sub> ] <sup>+</sup> <sup>b</sup>	-6.2	-4.0
MAD	2.0	1.9
MAX	6.2	4.0

<sup>a</sup> B3LYP means B3LYP/aug-cc-pVTZ <sup>b</sup> C<sub>3</sub>N<sub>2</sub>H<sub>3</sub> is the deprotonated imidazole ligand.

Table S9: Sequential Bond Dissociation Energies at 0 K excluding ZPE in kcal/mol: Deviation from B3LYP/aug-cc-pVTZ for the Large Molecules Test Set

molecule <sup>a</sup>	B3LYP <sup>b</sup>	B3LYP <sup>c</sup>	PBE <sup>c</sup>	DFTB3	B3LYP <sup>b</sup> //DFTB3 <sup>d</sup>
<i>Cu(I)</i>					
[Cu(-O-CH <sub>3</sub> ) <sub>1</sub> ]	202.5	+4.7	+13.5	+24.0	-0.5
[Cu(-O-CH <sub>3</sub> ) <sub>2</sub> ] <sup>-</sup>	77.7	+2.4	+3.4	-1.5	-1.0
[Cu(-S-CH <sub>3</sub> ) <sub>1</sub> ]	198.1	+2.8	+13.7	+6.6	-0.1
[Cu(-S-CH <sub>3</sub> ) <sub>2</sub> ] <sup>-</sup>	67.5	-0.4	+5.3	-6.5	-0.2
[Cu(-S-CH <sub>3</sub> ) <sub>3</sub> ] <sup>2-</sup>	-56.7	+0.6	+3.0	-10.4	-0.2
[Cu(HS-CH <sub>3</sub> ) <sub>1</sub> ] <sup>+</sup>	54.9	+1.3	+9.6	-3.0	-0.2
[Cu(HS-CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>	44.6	+1.3	+6.9	+0.5	+0.0
[Cu(HS-CH <sub>3</sub> ) <sub>3</sub> ] <sup>+</sup>	14.9	+0.5	+4.8	-1.5	-0.3
[Cu(HS-CH <sub>3</sub> ) <sub>4</sub> ] <sup>+</sup>	8.9	+0.9	+4.3	+3.7	-0.4
[Cu(N(=CH <sub>2</sub> )(CH <sub>3</sub> ) <sub>1</sub> ) <sup>+</sup>	63.7	+2.4	+9.5	+7.7	-0.5
[Cu(N(=CH <sub>2</sub> )(CH <sub>3</sub> ) <sub>2</sub> ) <sup>+</sup>	56.6	+1.7	+6.7	+9.6	-0.2
[Cu(N(=CH <sub>2</sub> )(CH <sub>3</sub> ) <sub>3</sub> ) <sup>+</sup>	13.9	+0.5	+4.0	+3.6	-1.7
[Cu(N(=CH <sub>2</sub> )(CH <sub>3</sub> ) <sub>4</sub> ) <sup>+</sup>	9.3	+0.4	+3.2	+3.1	-1.0
[Cu(S(CH <sub>3</sub> ) <sub>2</sub> ) <sub>1</sub> ] <sup>+</sup>	61.0	+1.2	+9.9	-2.6	-0.1
[Cu(S(CH <sub>3</sub> ) <sub>2</sub> ) <sub>2</sub> ] <sup>+</sup>	47.3	+1.1	+6.6	-0.1	-0.2
[Cu(S(CH <sub>3</sub> ) <sub>2</sub> ) <sub>3</sub> ] <sup>+</sup>	14.7	+0.3	+4.9	-1.3	-1.1
[Cu(S(CH <sub>3</sub> ) <sub>2</sub> ) <sub>4</sub> ] <sup>+</sup>	8.6	+0.4	+4.0	+4.1	-0.4
[Cu(C <sub>3</sub> N <sub>2</sub> H <sub>3</sub> ) <sub>1</sub> ] <sup>e</sup>	178.0	+2.0	+11.6	+31.8	-0.2
[Cu(C <sub>3</sub> N <sub>2</sub> H <sub>3</sub> ) <sub>2</sub> ] <sup>- e</sup>	80.1	+1.2	+3.8	+9.9	+0.0
[Cu(O=CH <sub>2</sub> ) <sub>1</sub> ] <sup>+</sup>	43.2	+1.6	+5.8	+4.2	-0.8
[Cu(O=CH <sub>2</sub> ) <sub>2</sub> ] <sup>+</sup>	42.2	+1.6	+6.0	+5.8	-0.5
[Cu(imidazole) <sub>1</sub> ] <sup>+</sup>	73.7	+2.4	+9.1	+12.2	-0.3
[Cu(imidazole) <sub>2</sub> ] <sup>+</sup>	62.7	+1.7	+6.3	+10.1	+0.0
[Cu(imidazole) <sub>3</sub> ] <sup>+</sup>	14.7	+0.7	+2.8	+1.4	-2.5
[Cu(imidazole) <sub>4</sub> ] <sup>+</sup>	10.7	+0.7	+3.3	+3.6	+1.1
Cu(-S-CH <sub>3</sub> )(N(=CH <sub>2</sub> )(CH <sub>3</sub> ))*	33.3	+0.5	+6.5	+6.2	-0.7
Cu(-S-CH <sub>3</sub> )* (N(=CH <sub>2</sub> )(CH <sub>3</sub> ))	167.8	+0.8	+10.7	+5.0	-0.3
[Cu(-S-CH <sub>3</sub> )(C <sub>3</sub> N <sub>2</sub> H <sub>3</sub> )] <sup>- e</sup>	64.1	+0.0	+3.5	+13.8	-0.3
[Cu(-S-CH <sub>3</sub> )* (C <sub>3</sub> N <sub>2</sub> H <sub>3</sub> )] <sup>- e</sup>	84.2	+0.7	+5.6	-11.4	-0.2
Cu(-S-CH <sub>3</sub> )(imidazole)*	35.7	+1.1	+4.4	+6.0	-0.5
Cu(-S-CH <sub>3</sub> )* (imidazole)	160.2	+1.4	+8.9	+0.3	-0.4
[Cu(-S-CH <sub>3</sub> )(HS-CH <sub>3</sub> ) <sub>1</sub> ] <sup>+</sup>	26.4	+0.3	+5.6	-4.1	-0.3
[Cu(-S-CH <sub>3</sub> )(HS-CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>	3.6	+0.3	+4.2	+3.1	-1.6
[Cu(C <sub>3</sub> N <sub>2</sub> H <sub>3</sub> )(imidazole) <sub>1</sub> ] <sup>e</sup>	45.1	+1.4	+4.2	+3.2	+0.0
MAD		1.2	6.3	6.5	0.5
MAX		4.7	13.7	31.8	2.5
<i>Cu(II)</i>					
[Cu(-O-CH <sub>3</sub> ) <sub>1</sub> ] <sup>+</sup>	489.5	+5.2	+22.3	+8.8	-1.2
[Cu(-O-CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>	214.2	+3.8	+10.8	+22.4	-0.3
[Cu(-S-CH <sub>3</sub> ) <sub>1</sub> ] <sup>+</sup>	492.8	+2.5	+22.0	-15.0	-0.4
[Cu(-S-CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>	188.6	+2.3	+12.6	+9.4	+0.3
[Cu(-S-CH <sub>3</sub> ) <sub>3</sub> ] <sup>-</sup>	45.1	+0.2	+2.3	+4.8	-0.5
[Cu(HS-CH <sub>3</sub> ) <sub>1</sub> ] <sup>2+</sup>	184.5	+0.8	+20.6	-15.9	-1.2
[Cu(HS-CH <sub>3</sub> ) <sub>2</sub> ] <sup>2+</sup>	78.3	+1.6	+10.8	+3.8	+0.6
[Cu(HS-CH <sub>3</sub> ) <sub>3</sub> ] <sup>2+</sup>	53.7	+0.7	+3.8	-3.7	-1.4
[Cu(HS-CH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup>	29.1	+1.1	+4.5	+3.3	+1.1
[Cu(N(=CH <sub>2</sub> )(CH <sub>3</sub> ) <sub>1</sub> ) <sup>2+</sup>	192.9	+1.9	+22.1	+1.6	-0.3
[Cu(N(=CH <sub>2</sub> )(CH <sub>3</sub> ) <sub>2</sub> ) <sup>2+</sup>	93.4	+1.7	+5.6	+9.3	-2.3
[Cu(N(=CH <sub>2</sub> )(CH <sub>3</sub> ) <sub>3</sub> ) <sup>2+</sup>	68.1	+1.0	+1.6	+0.1	+1.8
[Cu(N(=CH <sub>2</sub> )(CH <sub>3</sub> ) <sub>4</sub> ) <sup>2+</sup>	37.2	+1.0	+3.0	+0.2	-0.2
[Cu(S(CH <sub>3</sub> ) <sub>2</sub> ) <sub>1</sub> ] <sup>2+</sup>	212.9	-0.2	+19.2	-23.0	-3.1
[Cu(S(CH <sub>3</sub> ) <sub>2</sub> ) <sub>2</sub> ] <sup>2+</sup>	81.3	+1.8	+12.1	+3.5	+1.9
[Cu(S(CH <sub>3</sub> ) <sub>2</sub> ) <sub>3</sub> ] <sup>2+</sup>	50.1	+1.1	+4.4	+0.0	+0.1
[Cu(S(CH <sub>3</sub> ) <sub>2</sub> ) <sub>4</sub> ] <sup>2+</sup>	26.9	+0.8	+4.7	+4.6	-0.1
[Cu(C <sub>3</sub> N <sub>2</sub> H <sub>3</sub> ) <sub>1</sub> ] <sup>+ e</sup>	480.4	+3.6	+17.1	+10.3	-1.0
[Cu(C <sub>3</sub> N <sub>2</sub> H <sub>3</sub> ) <sub>2</sub> ] <sup>e</sup>	166.9	+1.5	+14.8	+36.6	+0.1
[Cu(O=CH <sub>2</sub> ) <sub>1</sub> ] <sup>2+</sup>	152.1	+1.6	+20.3	+0.5	-0.2
[Cu(O=CH <sub>2</sub> ) <sub>2</sub> ] <sup>2+</sup>	84.5	+1.6	+5.6	+3.5	-0.4
[Cu(imidazole) <sub>1</sub> ] <sup>2+</sup>	241.3	+4.1	+18.4	-8.2	-1.4
[Cu(imidazole) <sub>2</sub> ] <sup>2+</sup>	95.6	+2.1	+14.6	+26.5	+1.2
[Cu(imidazole) <sub>3</sub> ] <sup>2+</sup>	60.5	-1.1	-5.0	+6.5	-0.5
[Cu(-S-CH <sub>3</sub> )(N(=CH <sub>2</sub> )(CH <sub>3</sub> ))*] <sup>+</sup>	56.3	+1.9	+6.3	+9.3	-0.3
[Cu(-S-CH <sub>3</sub> )* (N(=CH <sub>2</sub> )(CH <sub>3</sub> ))] <sup>+</sup>	356.1	+2.6	+6.3	-7.1	-0.4
Cu(-S-CH <sub>3</sub> )(C <sub>3</sub> N <sub>2</sub> H <sub>3</sub> )* <sup>e</sup>	170.9	+2.2	+11.3	+35.7	+0.2
Cu(-S-CH <sub>3</sub> )* (C <sub>3</sub> N <sub>2</sub> H <sub>3</sub> ) <sup>e</sup>	183.2	+1.2	+16.4	+10.5	+0.8
[Cu(-S-CH <sub>3</sub> )(imidazole)*] <sup>+</sup>	65.9	+1.9	+6.6	+14.1	+0.1
[Cu(-S-CH <sub>3</sub> )* (imidazole)] <sup>+</sup>	317.3	+0.4	+10.3	+7.4	+1.2
[Cu(-S-CH <sub>3</sub> )(HS-CH <sub>3</sub> ) <sub>1</sub> ] <sup>+</sup>	45.3	+1.3	+6.6	-0.3	+0.0
[Cu(-S-CH <sub>3</sub> )(HS-CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>	19.5	+0.8	+6.3	+2.0	-0.8
[Cu(-S-CH <sub>3</sub> )(HS-CH <sub>3</sub> ) <sub>3</sub> ] <sup>+</sup>	8.7	+0.6	+4.2	+3.8	-0.8
[Cu(C <sub>3</sub> N <sub>2</sub> H <sub>3</sub> )(imidazole) <sub>1</sub> ] <sup>+ e</sup>	65.5	+1.8	+7.1	+14.1	-1.0
[Cu(C <sub>3</sub> N <sub>2</sub> H <sub>3</sub> )(imidazole) <sub>2</sub> ] <sup>+ e</sup>	20.6	+0.4	+7.6	+11.6	+0.5
MAD		1.7	10.5	9.6	0.8
MAX		5.2	22.3	36.6	3.1

<sup>a</sup> The non-dissociated molecule is listed. For unclear cases the ligand to dissociate is marked with a \*. Note that Cu(-S-CH<sub>3</sub>)(HS-CH<sub>3</sub>)<sub>3</sub>, Cu(C<sub>3</sub>N<sub>2</sub>H<sub>3</sub>)(imidazole)<sub>2</sub> and [Cu(imidazole)<sub>4</sub>]<sup>2+</sup> are excluded: the first two because of the very small bond dissociation energy, the last one due to the significant computing time that would be needed. For [Cu(imidazole)<sub>1</sub>]<sup>2+</sup>, while convergence could be reached within the Gaussian09<sup>3</sup> reference calculations using the quadratic convergence SCF method,<sup>4</sup> DFTB3 with our inhouse code could only converge with a finite electronic temperature. <sup>b</sup> basis set aug-cc-pVTZ <sup>c</sup> basis set 6-31+G(d) <sup>d</sup> B3LYP single point calculations on top of DFTB3 geometries. <sup>e</sup> C<sub>3</sub>N<sub>2</sub>H<sub>3</sub> is the deprotonated imidazole ligand.

Table S10: Gas Phase Proton Affinities at 0 K excluding ZPE in kcal/mol: Deviation from B3LYP/aug-cc-pVTZ for the Large Molecules Test Set

molecule <sup>a</sup>	B3LYP <sup>b</sup>	B3LYP <sup>c</sup>	PBE <sup>c</sup>	DFTB3	B3LYP <sup>b</sup> //DFTB3 <sup>d</sup>
<i>Cu(I)</i>					
[Cu(-S-CH <sub>3</sub> )(imidazole)]	329.8	-3.2	-5.1	+12.3	-0.2
[Cu(HS-CH <sub>3</sub> ) <sub>1</sub> ] <sup>+</sup>	218.6	-4.6	-8.6	-8.2	-0.3
[Cu(HS-CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>	236.7	-3.6	-7.2	-3.5	+0.0
[Cu(HS-CH <sub>3</sub> ) <sub>3</sub> ] <sup>+</sup>	248.1	-3.5	-6.6	-8.1	+1.2
[Cu(imidazole) <sub>1</sub> ] <sup>+</sup>	253.9	-3.3	-8.5	+0.5	-0.2
[Cu(imidazole) <sub>2</sub> ] <sup>+</sup>	271.5	-3.1	-6.4	+7.5	-0.1
[Cu(imidazole) <sub>4</sub> ] <sup>+</sup>	288.7	-2.8	-6.1	+9.8	+3.1
MAD		3.6	6.9	7.1	0.7
MAX		5.1	8.6	12.3	3.1
<i>Cu(II)</i>					
[Cu(-S-CH <sub>3</sub> )(imidazole)] <sup>+</sup>	253.1	-3.9	-10.6	-1.4	-0.0
[Cu(HS-CH <sub>3</sub> ) <sub>1</sub> ] <sup>2+</sup>	53.6	-5.0	-6.0	+0.4	-1.1
[Cu(HS-CH <sub>3</sub> ) <sub>2</sub> ] <sup>2+</sup>	86.5	-4.6	-1.7	+4.5	-0.4
[Cu(HS-CH <sub>3</sub> ) <sub>3</sub> ] <sup>2+</sup>	120.6	-4.6	-4.2	-1.0	-0.9
[Cu(HS-CH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup>	141.0	-4.0	-3.8	-1.5	+1.0
[Cu(imidazole) <sub>1</sub> ] <sup>2+</sup>	119.0	-3.1	-4.5	+1.7	-0.4
[Cu(imidazole) <sub>2</sub> ] <sup>2+</sup>	149.1	-2.8	+3.0	+14.1	+1.8
[Cu(imidazole) <sub>3</sub> ] <sup>2+</sup>	189.0	-4.3	-9.6	+9.0	+0.8
MAD		4.0	5.4	4.2	0.8
MAX		5.0	10.6	14.1	1.8

<sup>a</sup> The protonated form is listed. <sup>b</sup> basis set aug-cc-pVTZ <sup>c</sup> basis set 6-31+G(d) <sup>d</sup> B3LYP single point calculations on top of DFTB3 geometries.

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