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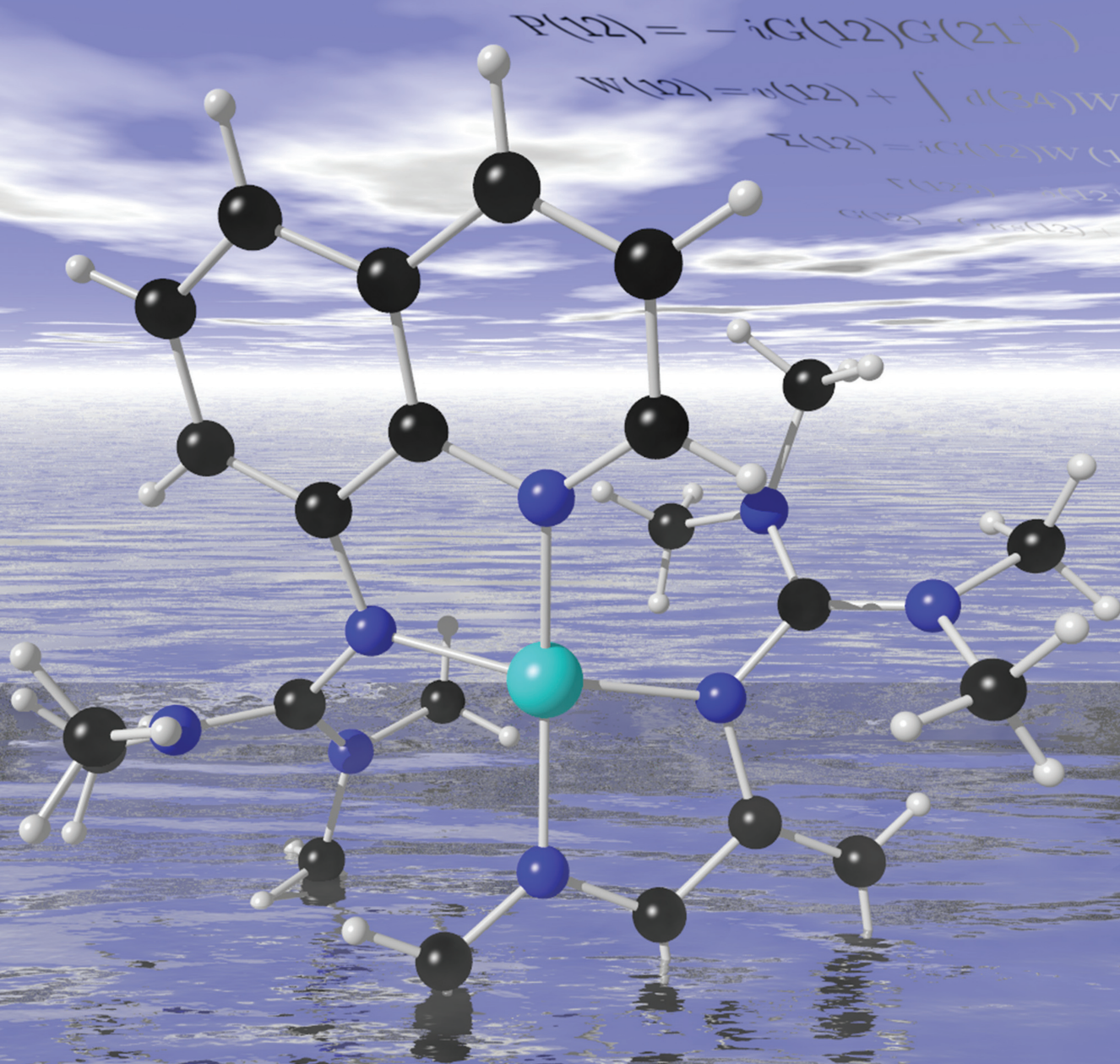
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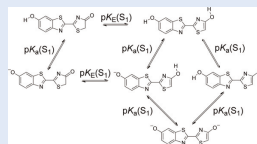
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Distinguishing between keto-enol and acid-base forms of firefly oxyluciferin through calculation of excited-state equilibrium constants

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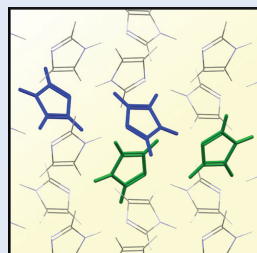
Aqueous keto-enol and acid-base excited-state equilibrium constants between six neutral, mono-anionic and di-anionic forms of oxyluciferin, the cofactor responsible for the bioluminescence of firefly luciferase, are for the first time calculated from free energies of a Born-Haber cycle, rather than using the Förster equation. The phenolate-keto-OxylH⁻ mono-anion is the preferred excited-state form of oxyluciferin in aqueous solution, attributing a potential key role to this species in firefly bioluminescence. DOI: 10.1002/jcc.23735



Exploiting space group symmetry in fragment-based molecular crystal calculations

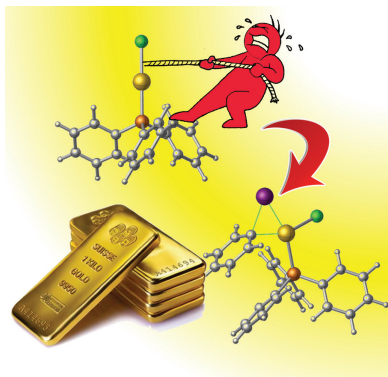
Greg Beran et al.

A simple algorithm for exploiting space group symmetry in fragment-based molecular crystal calculations not requiring a priori knowledge or implementation of the space group tables is described. It relies on rotating each monomer or dimer fragment to a common frame of reference for straightforward identification of symmetrically equivalent fragments. Exploiting space group symmetry often provides significant computational savings in accurate molecular crystal modeling. DOI: 10.1002/jcc.23737



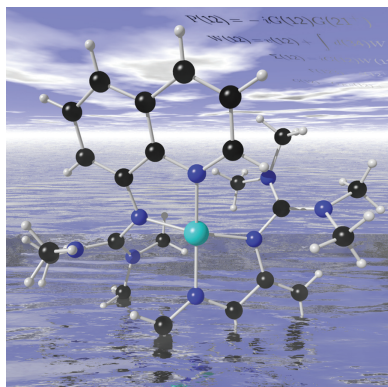
Activation Strain Model

Oxidative addition of aryl halides to gold(I) complexes are known to be kinetically sluggish. The reasons have so far not been understood. On page 2140, Israel Fernández, Lando P. Wolters, and F. Matthias Bickelhaupt provide the missing insight using the Activation Strain Model (ASM) of chemical reactivity. The relatively high rigidity of gold(I) complexes plays a key role. This rigidity, in combination with the fact that oxidative addition requires bending of the complex, leads to a high catalyst activation strain and thus a high activation energy. Based on this new insight, strategies are developed to achieve lower, more feasible reaction barriers.



TD-DFT

On page 2146, ground- and excited-state properties of copper(II) charge-transfer systems are investigated by Alexander Hoffmann, Martin Rohrmüller, Anton Jesser, Ines dos Santos Vieira, Wolf Gero Schmidt, and Sonja Herres-Pawlis starting from density-functional calculations with particular emphasis on the role of the exchange and correlation functional, the basis set, solvent effects, and the treatment of dispersive interactions. Furthermore, the applicability of TD-DFT to excitations of copper(II) bis(chelate) charge-transfer systems is explored by performing many-body perturbation theory (GW+BSE), independent-particle approximation (IPA) and Δ SCF calculations for a small model system containing simple guanidine and imine groups.



Geometrical and Optical Benchmarking of Copper(II) Guanidine–Quinoline Complexes: Insights from TD-DFT and Many-Body Perturbation Theory (Part II)

Alexander Hoffmann,^[a] Martin Rohrmüller,^[b] Anton Jesser,^[a] Ines dos Santos Vieira,^[c] Wolf Gero Schmidt,^[b] and Sonja Herres-Pawlis*^[a]

Ground- and excited-state properties of copper(II) charge-transfer systems have been investigated starting from density-functional calculations with particular emphasis on the role of (i) the exchange and correlation functional, (ii) the basis set, (iii) solvent effects, and (iv) the treatment of dispersive interactions. Furthermore (v), the applicability of TD-DFT to excitations of copper(II) bis(chelate) charge-transfer systems is explored by performing many-body perturbation theory (GW + BSE), independent-particle approximation and Δ SCF calculations for a small model system that contains simple guanidine and imine groups. These results show that DFT and TD-DFT in particular in combination with hybrid functionals are well suited for the description of the structural and optical properties, respectively, of copper(II) bis(chelate) complexes.

Furthermore, it is found an accurate theoretical geometrical description requires the use of dispersion correction with Becke–Johnson damping and triple-zeta basis sets while solvent effects are small. The hybrid functionals B3LYP and TPSSh yielded best performance. The optical description is best with B3LYP, whereby heavily mixed molecular transitions of MLCT and LLCT character are obtained which can be more easily understood using natural transition orbitals. An natural bond orbital analysis sheds light on the donor properties of the different donor functions and the intraguanidine stabilization during coordination to copper(I) and (II). © 2014 Wiley Periodicals, Inc.

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Introduction

Even with copper being an extremely important element in transition metal chemistry as well as playing a central role in many biological processes,^[1,2] most of the studies are centered on its oxidation state of +I. Cu(I) exhibits a rich coordination chemistry and possesses highly interesting photochemical properties such as charge-transfer excitations in visible range and emission with relatively long lifetime of about 1 μ s.^[3] Cu(II), conversely, possesses only limited significance from photophysical point of view due to its ultra-short lived lowest excited states.^[1] Another important field of research are electron transfer studies of Cu(II/I) systems due to relevance of copper-based redox-active metalloproteins.^[2] Contrary to the tendency of Cu(II) (d^9) to prefer a six- (distorted octahedral) or five-coordinate (square pyramidal or trigonal bipyramidal) geometry, and Cu(I) (d^{10}) mostly occurring as four-coordinate (tetrahedral),^[4,5] redox-active copper proteins exhibit more resembling geometry for both oxidation states, thus minimizing the required reorganizational energy for electron transfer reactions. Since the postulate of the “entatic state” by Vallee and Williams in 1968,^[6] low molecular weight Cu(II/I) systems have been investigated to model the coordination geometry and the electron transfer properties of enzymatic systems like the type 1 copper sites in blue copper proteins. And although more recent studies have challenged the concept of the “entatic state” as protein matrix derived distortion of the active site in favor of an electronic interpretation,^[7–11] the understanding of the influence of coordination geometry on elec-

tron transfer is still vital for inorganic and biochemical chemistry alike.^[12]

Guanidines are versatile N donor ligands with strong nucleophilicity, which coordinate main group as well as transition metals in various oxidation states.^[13–15] Copper-based guanidine complexes find application not only as biomimetic models for activation of dioxygen^[16,17] but also as polymerisation catalysts.^[18–22] In recent work from our group,^[12] a resonance Raman study on a pair of Cu(I) and Cu(II) guanidine–quinoline bis(chelate) complexes with highly interesting charge-transfer properties was performed to optically access the “entatic state,” the intermediate state of inner-sphere electron transfer. In a previous publication,^[23] we provided with an extensive theoretical study on the Cu(I) complex from this pair, which consisted of structural and optical benchmarking, as well as conformational and isomer

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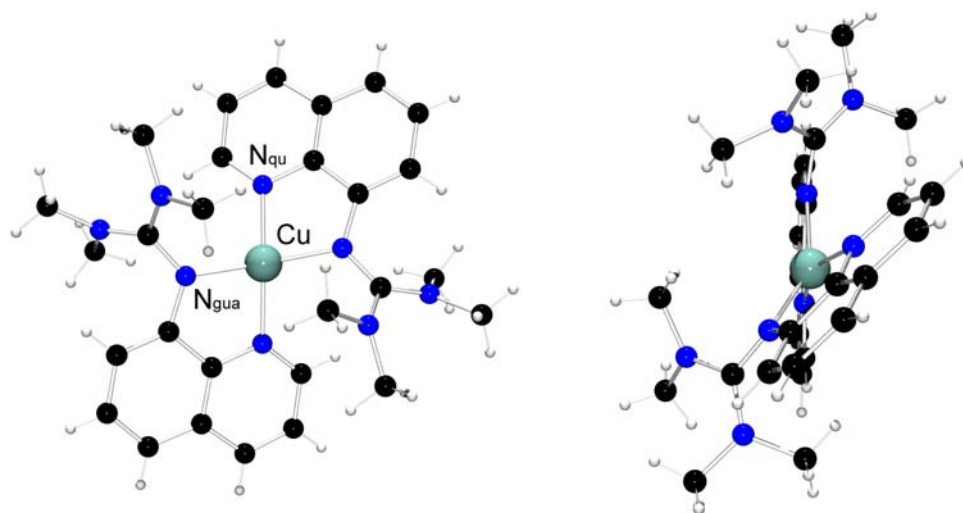


Figure 1. Molecular structure of $[\text{Cu}(\text{TMGu})_2]^{2+}$.

analysis at density functional theory (DFT) level of theory, with an emphasis on the amount of exact exchange used. To access the reliability of time-dependent DFT (TD-DFT) in describing charge-transfer states, many-body perturbation theory (MBPT) was used as a complementary method. The study showed that a reasonable agreement with experimentally obtained structures can be achieved with a local generalized-gradient approximation (GGA) like BP86. An amount of exact Hartree–Fock exchange is necessary to obtain agreement in optical spectra. MBPT calculations that solve the Bethe–Salpeter equation (BSE) based on quasiparticle (QP) energies obtained within the GW approximation, i.e., approximating the self-energy by the convolution of the single-particle propagator G and the screened Coulomb interaction W (see Ref. [24]), indicate that TD-DFT calculations based on a careful benchmarking with respect to the exchange–correlation functional and the basis set provide a qualitatively correct picture of the optical excitations in this class of molecules.^[23]

Here, we report on the guanidine–quinoline Cu(II) counterpart (Fig. 1). As shown in previous work, the choice of the basis set exhibits only a minor influence on the TD-DFT calculations, but we wanted to investigate when convergence is reached using a modern Ahlrichs quadruple-zeta basis sets. Moreover, we evaluated the influence of dispersion correction. At present, the ubiquitous dispersion interaction can be accounted for by performing high-level quantum-chemical wave function or quantum Monte Carlo methods or by the combination of exact exchange plus correlation energy within the adiabatic-connection fluctuation-dissipation theorem. In contrast, the currently used approximations to the electron exchange and correlation (XC) energy in DFT calculations—due to its numerical efficiency the method of choice for large molecules—do not properly describe the long-range van der Waals (vdW) interactions. Many concepts have been proposed to include dispersion interaction in DFT calculations to overcome this problem. “Seamless” van der Waals density-functional (vdW-DF) approaches^[25,26] allow for a first-principles description of dispersion interaction. The addition of a pairwise interaction energy approximately C_6R^{-6} with a suitable cutoff function for small

atomic distances R (see for example, Refs. [27–30]) is computationally inexpensive. This so-called DFT-D scheme may be refined by introducing an electron density dependence in the C_6 coefficients,^[31] and delivers information on the influence of vdW forces at virtually no additional computational costs. In the current DFT-D3 implementation, Grimme included pairwise-specific dispersion coefficients and a set of cutoff radii, both calculated *ab initio*.^[32] This approach is used here in conjunction with Becke–Johnson damping that seems to provide a physically correct short-range description of the electron correlation even with unmodified standard functionals.^[30] This model has recently been applied to various challenging problems such as electron transfer,^[33] agostic interactions,^[34] and transorganometallic species.^[35]

Substantial effort is also devoted here to the description of the molecular optical response. Thereby, the benchmarking focusses on the amount of exact exchange in the used functional. In addition to the gas-phase calculations an extensive series of solvation modelled (TD)-DFT einheitliche Schreibweise von TD-DFT with a wide range of solvent polarities was conducted for the Cu(II) complex as well as for the Cu(I) complex. The coordination of the copper center is not rigid in solution—alterations in bond length and the coordination geometry can occur due to solvent-induced changes in polarisation. Dependency of charge-transfer properties on coordination geometry has been reported in several studies.^[36] Furthermore, special attention was paid to donor–acceptor effects between ligands and complexes. Here, natural bond orbital (NBO) theory has been applied.^[37–39] In addition to these studies on the large guanidine–quinoline copper(II) system, MBPT, independent-particle approximation (IPA) as well as self-consistent field (Δ SCF) calculations are applied to a small model system to assess the applicability of adiabatic linear-response TD-DFT to optical charge-transfer transitions in these copper(II) complexes.

Theoretical Methods

The geometry of the complex cations $[\text{Cu}(\text{TMGu})_2]^{2+}$ and $[\text{CuN}_8\text{C}_8\text{H}_{16}]^{2+}$ (termed guanidine–quinoline (GQ) Cu(II) and

Table 1. Becke–Johnson damping factors.

Functional	S8	a1	a2	Reference
B3LYP	1.9889	0.3981	4.4211	[30]
TPSSH	2.2382	0.4529	4.6550	Grimme (private communication) ^[a]
BHLYP	1.0354	0.2793	4.9615	[57]
TPSS	1.9435	0.4535	4.4752	[30]

[a] For TPSSH, not the values of the paper were used. These corrected values have been kindly provided by S. Grimme as private communication.

Cu(II) model, respectively, in the following) are fully optimized at different levels of density-functional theory using the Berny algorithm as implemented in Gaussian09.^[40] All optimized geometries are characterized as stationary points on the potential energy surface with vibrational frequency calculations. TD-DFT calculations are performed on the equilibrium ground state geometries with different density-functional theory levels. The Gaussian09 calculations are performed with the local GGA PW91^[41–43] and M06-L,^[44] the nonlocal hybrid GGAs B3LYP,^[45–48] the local meta GGA TPSS,^[49] and the nonlocal hybrid meta GGA TPSSH^[49] combined with the def2-SVP, def2-TZVP, or def2-QZVP basis set.^[50] Continuous spectra are plotted with the SWizard program^[51,52] using Gaussian functions with an average half band width of 3000.0 cm^{−1} or with the AOMix program.^[52,53] Solvent models have been used as implemented in Gaussian09.^[40] Some of these calculations have been performed within the MoSGrid environment.^[54,55]

As dispersion correction, we used the standard Grimme dispersion (named as D2^[56] and D3^[32,57]) as implemented in Gaussian, Revision D.01. The Becke–Johnson dispersion was also used as implemented in Gaussian, Revision D.01 with the parameters for the functionals given in Table 1.

To check the basis set convergence, calculations using a plane wave basis are performed additionally for some configurations. A complete set is formed by an infinite number of plane waves and a plane-wave basis converges in a smooth, monotonic manner to the target wavefunction. It allows, thus, for calculations of arbitrary accuracy by increasing the number of basis functions. The convergence of the calculation can be monitored by varying the plane-wave cutoff. An energy cutoff of 380 eV is found to lead to converged results for the calculations presented here. Moreover, as all functions in the plane-wave basis are mutually orthogonal and are not associated with any particular atom, plane-wave basis sets do not exhibit basis set superposition error. These results were obtained using the Vienna *Ab initio* Simulation Package (VASP).^[58] Periodic boundary conditions are used for the calculations with a 16 × 16 × 16 Å³ supercell.

Optical spectra are not only calculated using the adiabatic approximation to linear-response TD-DFT but for the Cu(II) model system also on the IPA level of theory^[59] as well as by performing MBPT calculations that solve the BSE based on QP energies obtained within the GW approximation.^[24] IPA calculations while not taking many-body electron–electron and electron–hole interactions into account, typically allow for the qualitative description of optical absorption peaks and their intuitive interpretation in terms of single-particle states. MBPT is often considered as the most successful approach to overcome

the limitations of TD-DFT. Thereby, one considers the screening response of the electronic system after electronic or optical excitation. Accordingly, the dynamically screened or shielded Coulomb interaction *W* is the central quantity used in these methods. The excitation energies correspond to the poles of single- and two-particle Green functions. In condensed-matter physics, it is frequently used to describe excitons in periodic systems. Optical response calculations based on the BSE for inorganic semiconductors typically result in spectra that resemble closely the experiment, concerning both line shape and excitation energies, with deviations below one or two tenths of 1 eV.^[60,61] Calculations for systems with stronger charge inhomogeneities like for example molecular crystals tend to lead to larger deviations of up to several tenths of 1 eV with respect to experimental data.^[62,63] However, there is also an increasing number of MBPT theory applications to excitations in finite, molecular systems, see, for example, Refs. [64,65]. The foundations of the methodology, as well as implementational issues and possible pitfalls with respect to molecular applications are discussed in Ref. [66]. Technically, we use the VASP implementation for performing the QP calculations in GW approximation.^[67] Thereby, the screening is calculated from first principles within the random-phase approximation. QP energies are calculated using a cutoff energy of 100 eV and 128 frequency points. The time-evolution-based approach developed by one of the present authors^[68] is used for solving the BSE. Thereby, a static BSE kernel is used within as well as beyond the Tamm–Dancoff approximation,^[69] that is, neglecting or accounting for resonant–antiresonant coupling terms in the electron–hole Hamiltonian, see, for example, Refs. [69,70]. Thereby, all electron–hole pairs within an energy window of 18 eV are taken into account. The calculations are on the same footing as in our previous studies.^[23,71] Finally, we perform Δ SCF calculations for the energetically lowest optical excitation, that is, derive its energy from two separate self-consistent-field calculations, see, for example, Ref. [72]. This approach fully accounts for electronic relaxation and allows for a numerically efficient yet often very accurate modeling of single, well-defined excitations.

Results and Discussion

Structural benchmarking

With the hybrid guanidine–quinoline ligand TMGqu molecular structures of the Cu(II) complexes [Cu(TMGu)₂][TfO]₂ and [Cu(TMGu)₂][PF₆]₂ have been obtained experimentally from crystal structures.^[12] The correct description of the donor competition can be rather challenging,^[23,73] such that we focus on

Table 2. Selected bond lengths (Å), angles (°), and structural parameter τ_4 ^[76] of the [Cu(TMGu)₂]²⁺ dication.

	Dispersion	Cu—N _{gua}	Cu—N _{qu}	τ_4	CuN ₂ , CuN' ₂
Experimental average ^{[12], [a]}		1.963	1.975	0.41	43.6
Experimental extremes ^{[12], [a]}		1.959(2)–1.964(3)	1.967(3)–1.980(3)	0.40–0.41	42.5–44.6
B3LYP/def2-SVP	–	2.022	2.028	0.46	49.7
B3LYP/def2-SVP	GD2	1.994	2.015	0.40	42.6
B3LYP/def2-SVP	GD3	1.998	2.013	0.43	46.2
B3LYP/def2-SVP	GD3BJ	1.993	2.010	0.43	46.7
B3LYP/def2-TZVP	–	2.018	2.015	0.46	50.1
B3LYP/def2-TZVP	GD2	1.989	2.002	0.39	42.4
B3LYP/def2-TZVP	GD3	2.000	1.993	0.43	46.3
B3LYP/def2-TZVP	GD3BJ	1.989	1.998	0.44	46.7
B3LYP/def2-QZVP	–	2.016	2.013	0.46	50.0
B3LYP/def2-QZVP	GD3	1.992	1.999	0.43	46.1
B3LYP/def2-QZVP	GD3BJ	1.988	1.996	0.43	46.6
TPSSH/def2-SVP	–	2.010	2.013	0.46	49.9
TPSSH/def2-SVP	GD3BJ	1.985	2.013	0.45	48.0
TPSSH/def2-TZVP	–	1.999	1.996	0.46	50.3
TPSSH/def2-TZVP	GD3BJ	1.976	1.983	0.44	47.8
TPSSH/def2-QZVP	–	1.999	1.995	0.46	50.1
M06L/def2-SVP	–	2.004	2.020	0.43	46.9
M06L/def2-SVP	GD3	2.002	2.019	0.43	47.2
M06L/def2-TZVP	–	2.001	2.005	0.43	46.2
M06L/def2-TZVP	GD3	1.999	2.005	0.43	46.4
TPSS/def2-TZVP	–	1.866	1.881	0.38	40.6
TPSS/def2-TZVP	GD3BJ	1.853	1.869	0.39	41.2
PW91/def2-SVP	–	2.022	2.014	0.48	53.3
PW91/def2-TZVP	–	2.017	1.997	0.49	53.2

[a] For the regarded cation, two experimental structures are known.^[12] The crystallographic mean deviation adds to the extreme values of the two structures. Statistically, the experimental average is most useful for reasons of comparison.

the interplay of guanidine and quinoline units. The quinoline is in general a softer donor, whereas the guanidine is slightly harder but being able to coordinate copper in all oxidation states.^[12,14,16,74] Moreover, the guanidine unit is sterically very encumbering. In previous work,^[23,75] we found that hybrid functionals such as B3LYP, TPSSH, and pure functionals such as M06-L and PW91 give a sufficient quality in structure prediction. Sufficient quality is reached when the DFT yields a structure which is within the error bar of the average of the experimental structures.^[23] Evaluation of the dispersion influence has shown that for copper(II) bis(chelate) complexes B3LYP and TPSSH with DFT-D3 and Becke–Johnson damping are the most favorable choices.^[75] Table 2 collects all data of the geometry optimizations of [Cu(TMGu)₂]²⁺ with the functionals B3LYP, TPSSH, TPSS, M06-L, and PW91 using Ahlrichs basis sets and different types of dispersion.

The correct description of the Cu—N bond lengths in relative and absolute values is not trivial and some functionals predict the crucial bond lengths too short (TPSS) or too long (PW91 and M06-L). This is not remedied substantially by including dispersion corrections. The hybrid functionals B3LYP and TPSSH perform slightly better (Table 2, Fig. 2) but only when dispersion correction is applied the structural agreement is convincing (Fig. 3). In addition, the coordination environment is not only defined by the Cu—N bond lengths but also by the angle between the chelate planes CuN_{qu}N_{gua} and the so-called τ_4 -value which determines the degree of distortion between tetrahedral and square-planar environment.^[76] A

value of 1 indicates an ideal tetrahedron, whereas 0 assigns a square-planar geometry. It has to be noticed that the dispersion corrections also ameliorate the prediction of the τ_4 value and the angle between the chelate planes (CuN₂, CuN'₂). Only together with the correct Cu—N bond lengths these values can be regarded as valuable indicators for the coordination sphere description.

Figure 2 summarizes the basis set influence and reveals that the bond lengths do not change significantly between using the triple-zeta def2-TZVP basis set and its quadruple-zeta relative. Hence, the structural convergence is reached here and for

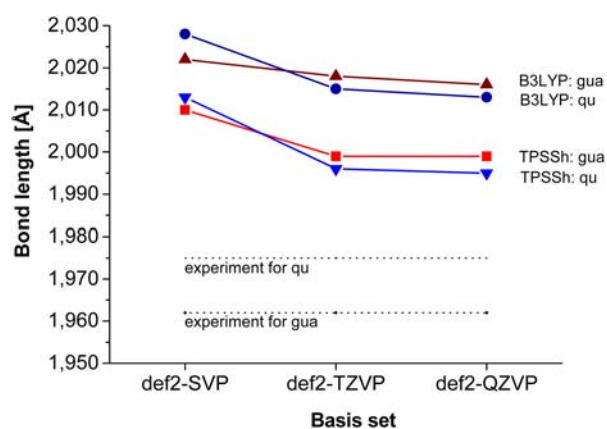


Figure 2. Dependence of Cu—N bond lengths on basis set quality and functional for [Cu(TMGu)₂]²⁺.

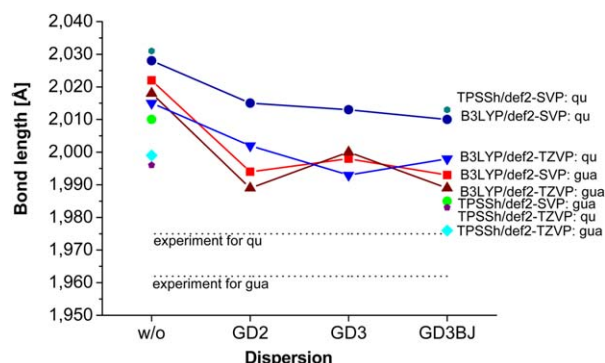


Figure 3. Dependence of Cu–N bond lengths on the inclusion of dispersion correction for $[\text{Cu}(\text{TMGu})_2]^{2+}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

further calculations, triple-zeta quality is sufficient. Using TPSSH or B3LYP with the def2-TZVP basis set and D3 dispersion with Becke–Johnson damping, the accuracy of the crystallographically determined structures is achieved (error in Cu–N bond lengths: 0.012 Å, 0.5% of bond lengths).

The canonical molecular orbitals of the $[\text{Cu}(\text{TMGu})_2]^{2+}$ dication have been analyzed (B3LYP/def2-TZVP, Fig. 4). The frontier orbitals mainly consist of π and π^* orbitals of the ligands sometimes mixed with d orbital contributions. These are degenerate pairs (A and B symmetry of the C_2 point group) of spin orbitals because of the unrestricted treatment. The first four unoccupied α -spin molecular orbitals (MOs) consist of π^* orbitals of the quinolines, whereas the fifth and sixth

are of guanidine π^* nature. The occupied α -spin MOs show quinoline π character for the first two MOs and guanidine π character for the third and fourth. The β -spin lowest unoccupied MO (LUMO) in contrast is a Cu d orbital of A symmetry and antibonding nature in respect to the Cu–N bonds. It shows the same form as the highest occupied MO (HOMO) of the corresponding $[\text{Cu}(\text{TMGu})_2]^+$ monocation^[23] thus complying nicely with the $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ oxidation. The α -spin counterpart, the d-orbital-based singly occupied MO, is found in the orbitals HOMO-4 and HOMO-6, as a linear combination with a quinoline π MO of A symmetry.

Optical benchmarking

For a meaningful study of electronic structure and excited states behavior of $[\text{Cu}(\text{TMGu})_2]^{2+}$, a reliable theoretical description is required. Therefore, a TD-DFT benchmarking of density functionals compared to the experimental absorption spectrum was accomplished. The GGA functionals PW91 and M06-L, the meta GGA TPSS as well as the hybrid functionals B3LYP and TPSSH were used. The functionals without Hartree–Fock (HF) exchange predict too low excitation energies by 0.5–0.7 eV in average (Fig. 5) and are not suitable for the description of electronic transitions of copper complexes with guanidine hybrid ligands, as also shown in previous work for the $\text{Cu}(\text{I})$ complex.^[23,75] The hybrid functionals B3LYP and TPSSH yield accurate predictions for all experimental bands (deviation from experimental values below 0.3 eV). The well-

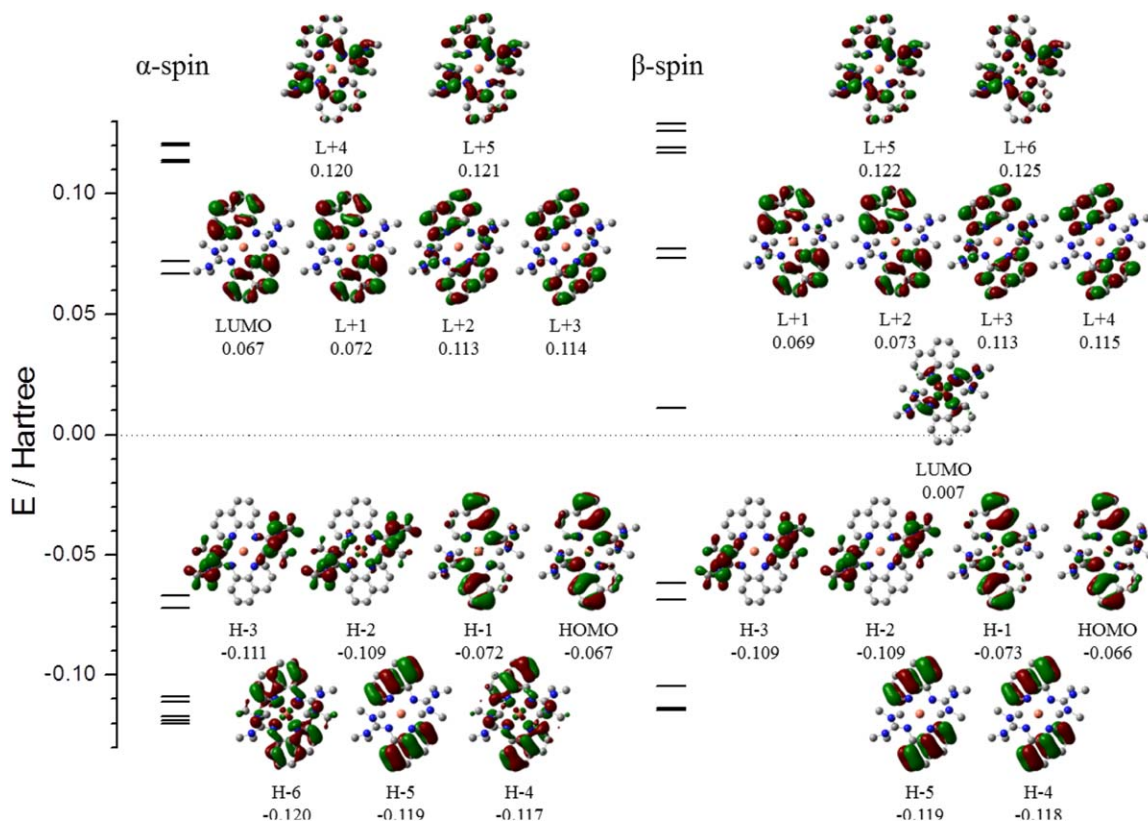


Figure 4. Frontier orbitals of the $[\text{Cu}(\text{TMGu})_2]^{2+}$ complex cation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

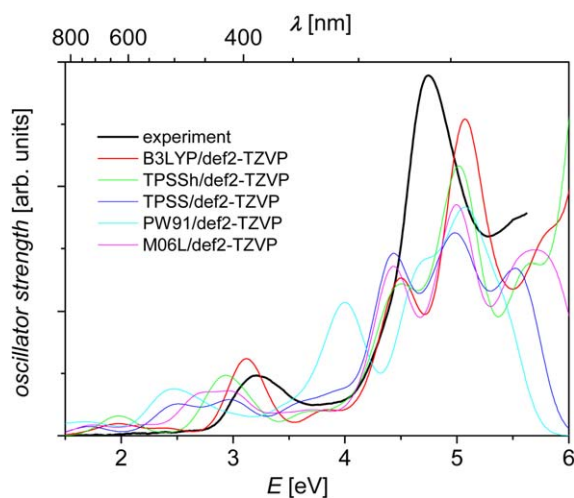


Figure 5. Density-functional benchmarking of the $[\text{Cu}(\text{TMGu})_2]^{2+}$ complex cation absorption spectra. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

performing hybrid functional B3LYP (deviation below 0.1 eV) was chosen for further calculations (for a more detailed discussion of single transitions vide infra). Thus, comparability to previous work on the analogous Cu(I) complex is given.

Special attention has been paid to the dispersion influence. As dispersion correction GD3 with Becke–Johnson damping yielded the best structural results, the optically best behaving functionals TPSSh and B3LYP have been tested toward the dispersion influence (Fig. 6). Here, it appears that the dispersion has no influence and the fine accordance to the experimental data persists. This is consistent with the behavior for the analogous Cu(I) complex.^[75] It should be noticed that the effect of the dispersion correction on the UV spectra is just an effect of slightly different geometries (resulting from the dispersion correction) used for the TD-DFT calculations and no electronic effect.

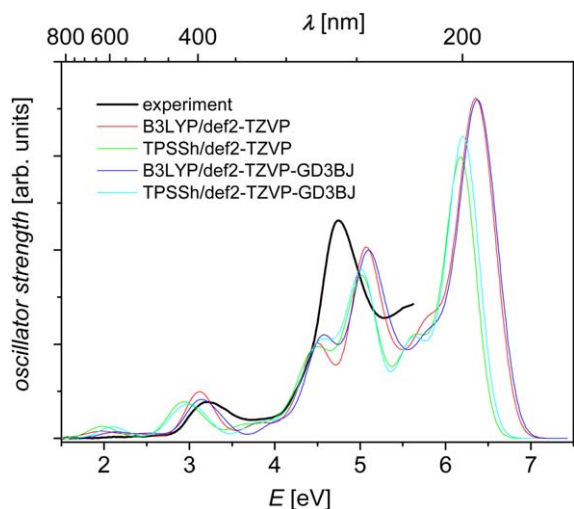


Figure 6. Calculated absorption spectra of $[\text{Cu}(\text{TMGu})_2]^{2+}$ with the TPSSh and B3LYP functionals with and without dispersion corrections in comparison to experimental data. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

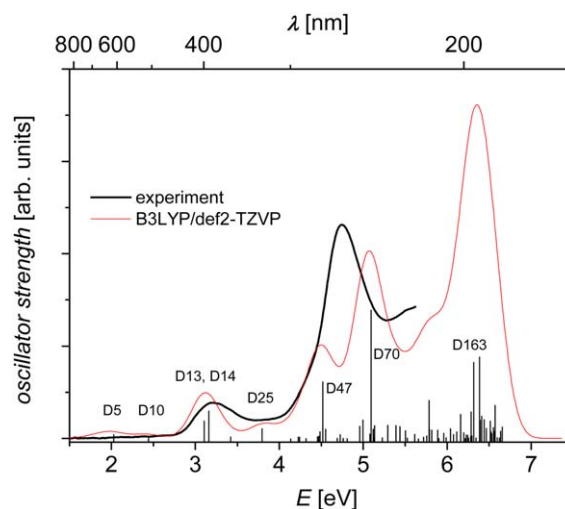


Figure 7. Experimental (black) and theoretical absorption spectra of the $[\text{Cu}(\text{TMGu})_2]^{2+}$ complex cation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The resulting theoretical absorption spectrum has been compared to experimental UV–Vis results (Fig. 7). The experimental spectrum is dominated by two bands. In theory, the band at 387 nm (3.2 eV) is well predicted by the transitions D13 and D14 at 3.08 and 3.13 eV. The band at 261 nm (4.8 eV) corresponds to the intensive transitions D47 and D70 at 4.48 and 5.07 eV which cannot be resolved experimentally. In addition, two transitions at lower energies are predicted, D5 at 2.00 eV and D10 at 2.42 eV. In experiment, there is a weak absorption between 450 and 600 nm, with much smaller absorption coefficients of $300\text{--}1000\text{ M}^{-1}\text{ cm}^{-1}$. In the hard UV region more intensive bands are predicted due to ligand–ligand charge-transfer processes which cannot be observed experimentally as the solvent absorption starts already here.

The assignment of the absorption bands to electronic transition types is complicated not only by several contributing donor–acceptor orbital pairs but also by the unrestricted treatment resulting in α - and β -spin one-electron orbitals. With the help of natural transition orbital (NTO) analysis some clarity shall be given.^[77]

Of the intensive transitions, D5, D10, and D25 have been assigned to unambiguous donor–acceptor orbital pairs. For D13, D14, D47, and D70 even with NTO analysis several donor–acceptor pairs have been found. For the important transitions TD-DFT results, NTO eigenvalues and assignment are listed in Table 3. The NTOs are shown in Figure 8.

The transitions D5, D10, D13, D14, and D25 have all one acceptor orbital in common, which corresponds to the β -LUMO with Cu d character. The donor orbitals of D5 and D25 both show electron density on the metal in addition to quinoline and guanidine (D25) involvement. Thus, D5 and D25 are assigned to be a mixture of ligand field d–d transition and ligand-to-metal charge-transfer (LMCT). Because the acceptor orbital exists only with β -spin, D5 and D25 are pure β -spin excitations. The donor orbital of the D10 transition is a pure guanidine π orbital which renders the D10 a β -spin LMCT transition.

Table 3. Natural Transition Orbitals (NTO) analysis of the $[\text{Cu}(\text{TMGqu})_2]^{2+}$ complex cation.

State	λ (nm)	E (eV)	f (10^{-4})	Assignment	NTO
D5	621	2.00	238	LF/LMCT	0.98 (β)
D10	513	2.42	117	LMCT	0.98 (β)
D13a	403	3.08	722	LMCT	0.41 (β)
D13b				LC	0.24 (α), 0.28 (β)
D14a	396	3.13	903	LMCT	0.58 (β)
D14b				LC	0.21 (α), 0.20 (β)
D25	327	3.80	419	LF/LMCT	0.88 (β)
D47a	277	4.48	1769	LC	0.31 (α , β)
D47b				LC	0.17 (β) ^[a]
D70a	245	5.07	4262	LC	0.26 (α)
D70b				LC/LMCT	0.16 (α)
D70c				LC	0.13 (β)
D70d				LC/LMCT	0.11 (β) ^[a]

[a] Other contributions are < 0.1 .

For D13 and D14 both the NTO analyses yield two donor–acceptor pairs, whereas the involved orbitals are identical, only the NTO eigenvalues are slightly different. The eigenvalue sums of the identical orbital pairs are equal to almost one, which means that D13 and D14 are combinations of two independent electronic transitions, which are close in energy and thus mixed by the TD-DFT. The NTO analysis reaches its limits in this case. The first transition (a) involved in D13 and D14

stems from a donor orbital with mixed ligand character. The acceptor orbital is the β -LUMO. Thus, this transition is a pure β -spin LMCT. The second transition (b) has equal parts in α - and β -spin and corresponds to α -spin HOMO–LUMO transition. Both donor and acceptor orbital are of quinoline character, with additional electron density on the coordinating guanidine N atom for the donor orbital, thus this transition is assigned to a ligand-centered (LC) excitation.

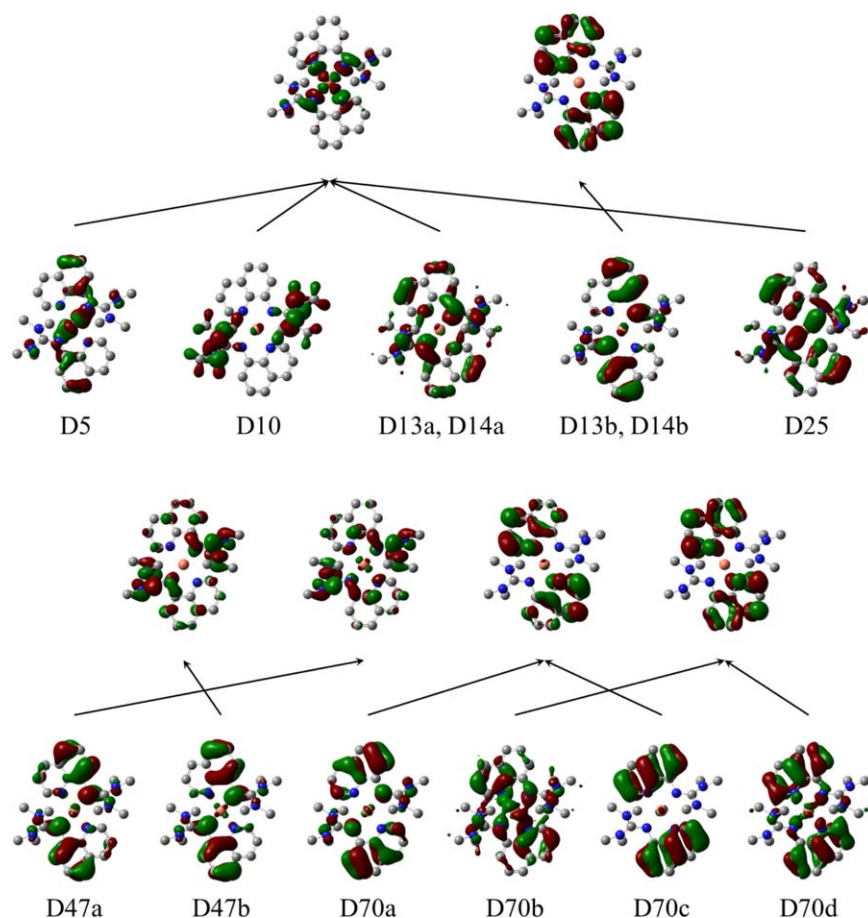


Figure 8. NTOs for the important transitions of the $[\text{Cu}(\text{TMGu})_2]^{2+}$ complex cation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 4. Selected structural parameters of the $[\text{Cu}(\text{TMGqu})_2]^+$ and $[\text{Cu}(\text{TMGqu})_2]^{2+}$ cations at various solvation models (B3LYP/def2-TZVP).

	Gas phase	PCM THF	SMD THF	PCM MeCN	SMD MeCN	PCM water	SMD water
$[\text{Cu}(\text{TMGqu})_2]^+$							
Cu–N _{gua} [Å]	2.178	2.164	2.232	2.165	2.233	2.165	2.175
Cu–N _{qu} [Å]	2.048	2.051	2.055	2.051	2.057	2.051	2.073
$\angle(\text{CuN}_2\text{CuN}_2)$ [°]	76.7	73.7	75.8	73.7	75.6	73.8	67.0
$[\text{Cu}(\text{TMGqu})_2]^{2+}$							
Cu–N _{gua} [Å]	2.018	2.010	2.020	2.012	2.024	2.014	2.019
Cu–N _{qu} [Å]	2.015	2.014	2.032	2.015	2.044	2.015	2.055
$\angle(\text{CuN}_2\text{CuN}_2)$ [°]	49.9	50.2	47.3	48.8	47.6	48.4	49.1

For D47, two donor–acceptor pairs have been found. The donor NTOs comply to the degenerate HOMO and HOMO-1 with quinoline character, and the acceptor NTOs comply to the degenerate LUMO+4 and LUMO+5 with guanidine character (as for α -spin). Thus, D47 is a combination of LC quinoline–guanidine excitations which differ only in symmetry.

D70 shows the highest degree of orbital mixing. Even with NTO analysis, no unambiguous assignment can be made. The first four donor–acceptor pairs will be discussed. The first two pairs (a, b) are of α -spin, the third (c) and the fourth (d) are β -spin. The acceptor NTOs are easily identified as the degenerate LUMO and LUMO+1 (as for α -spin). For the donor NTOs, the assignment is much more complicated. The donor orbital of D70 (a) is similar to the α -spin HOMO-4, which is a mixture of quinoline π orbitals and the Cu d SOMO. The D70 (d) donor orbital again shows some similarity to the α -spin HOMO-6, but possesses B symmetry, whereas α -HOMO-6 is A symmetrical. In addition, D70 (d) is a β -spin only transition, which means that the metal character of the donor NTO stems from lower lying d orbitals. Same applies to the D70 (b) donor orbital, which is of B symmetry and thus cannot originate from any mixings involving the SOMO. The D70 (c) donor NTO consists simply of lower lying quinoline π orbitals. Thus, D70 is a combination of LC and mixed LC/LMCT excitations.

Application of solvation models

As standard, we optimize the molecules in gas phase but with regard to the charge stabilization of cations (such as $[\text{Cu}(\text{TMGqu})_2]^+$) and dications ($[\text{Cu}(\text{TMGqu})_2]^{2+}$) the geometrical changes during optimization within a solvent need to be addressed. Especially for correct treatment of excited states,^[12] the solvent influence needs to be investigated. Hence, the structure of the $[\text{Cu}(\text{TMGqu})_2]^+$ cation was optimized with the integral-equation-formalism polarizable continuum model (IEF-PCM) for several solvents: the relatively unpolar tetrahydrofuran (THF, $\epsilon = 7.4257$), the polar acetonitrile (MeCN, $\epsilon = 35.688$), and the strongly polar water ($\epsilon = 78.3553$). Moreover, we used as well a charge-density (D) based solvation model (SM) called the SMD model, developed for accurate calculations of solvation free energies of neutral molecules and ions. For ease of comparison, we have performed this study only with the B3LYP/def2-TZVP method.

Due to solvation, slight changes in Cu–N bond lengths are predicted (Table 4). Interestingly, the choice of solvent does not

yield a large influence when using the IEF-PCM. The Cu–N_{qu} bond lengths change only slightly (+0.003 Å), and the Cu–N_{gua} bond lengths decrease by 0.013 Å. The plane angle decreases by 3°. Thus, with the IEF-PCM, the structural parameters are *de facto* independent of solvent. With the SMD model, the optimized structures in acetonitrile and in tetrahydrofuran are very similar. Compared to the gas-phase structure, the Cu–N_{qu} bond lengths increase by 0.008 Å. Contrary to the IEF-PCM model the Cu–N_{gua} bond lengths show a large increase by 0.055 Å. The plane angle decreases slightly by 1°. For water, the Cu–N_{gua} bond lengths are equal to gas phase (–0.003 Å), but a larger change is predicted for the Cu–N_{qu} bond lengths which increase by 0.025 Å. The plane angle decreases by about 10° showing a considerable flattening of the already distorted tetrahedron.

For the $[\text{Cu}(\text{TMGqu})_2]^{2+}$ cation the IEF-PCM model yields overall almost the same structure as the gas-phase calculation with the highest deviation of the Cu–N_{gua} bond lengths (–0.003 Å) in tetrahydrofuran. The SMD calculations yield larger deviations for the Cu–N_{qu} bond lengths (+0.029 Å in acetonitrile and +0.040 Å in water) but still give structures very similar to gas phase.

After optimization in solvent models, TD-DFT was accomplished for both complexes: it yields for $[\text{Cu}(\text{TMGqu})_2]^+$ cation almost solvent-independent spectra (Supporting Information

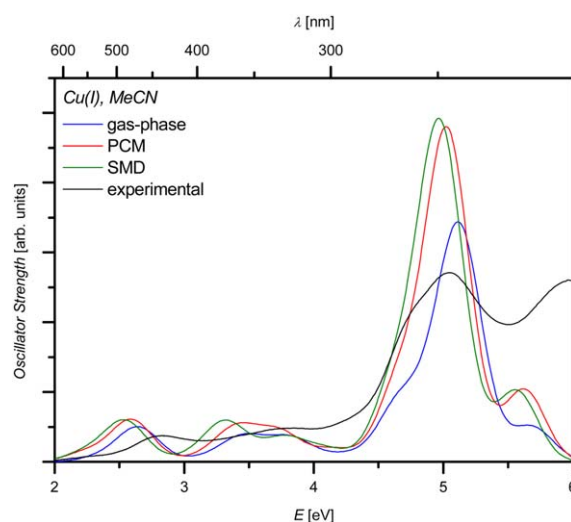


Figure 9. TD spectra for the $[\text{Cu}(\text{TMGqu})_2]^+$ cation with both solvation models in acetonitrile compared to gas-phase and experimental spectra. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

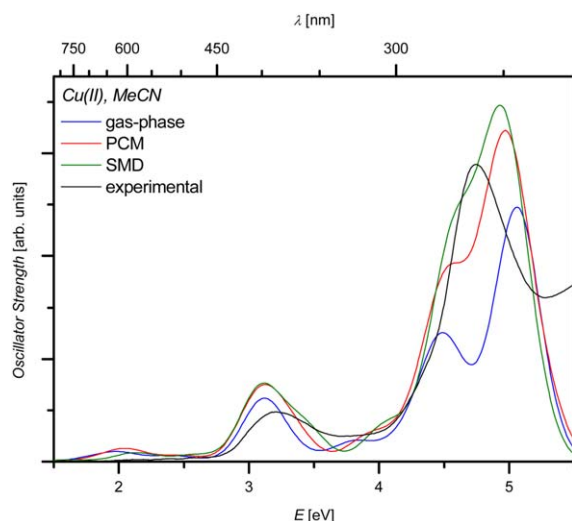


Figure 10. TD spectra for the $[\text{Cu}(\text{TMGqu})_2]^{2+}$ cation with both solvation models in acetonitrile compared to gas-phase and experimental spectra. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figs. S1 and S2). This is explained by the highly similar ground state structures. The only exception is the SMD water calculation, which yields small structural deviations from other SMD calculations resulting in minor band shifts (Supporting Information Fig. S2, at 3.5 eV). The small influence of the solvation models is summarized in Figure 9 for MeCN and Supporting Information Figure S3 for THF: Compared to the gas-phase calculation, the absorption bands are slightly shifted to lower energies, with a larger shift for the SMD model. In addition, the intensities of the bands are increased. Overall, the agreement with the experiment is not enhanced with the use of a solvation model. However, the deviation is not of qualitative nature. The prediction of the relative intensity and relative positions of the bands is correct, only the absolute energies are shifted by approximately the same value.

For the $[\text{Cu}(\text{TMGqu})_2]^{2+}$ cation, the TD-DFT spectra with the IEF-PCM model are similar to the gas-phase spectra (Supporting Information Figs. S4–S6 and Fig. 10). The absolute energies of the bands are not changed, only the intensities are slightly higher. The choice of solvent shows no influence. With the SMD model, only minor changes arise such as a shoulder at 3.5 eV due to a larger shift to higher energies of the LMCT transition and a unification of the two intensive bands in the UV range (as predicted in gas phase) to a single one (as observed in the experiment). Thus, the SMD model yields better accordance to experimental UV spectra concerning the band shapes, whereas the energies and the intensities are predicted reasonably by the gas-phase calculations.

NBO analysis

After inspection of the canonical orbitals a dissection of more localized orbitals can bring deeper insight into the inherent electronic structure of the copper complexes. The NBO analysis has been developed by Weinhold and coworkers^[37,38] as a convenient method to describe hybridization and covalence

effects of molecules. NBOs are attained by several transformations starting from the basis atomic orbitals (AOs). First the basis AOs are transformed to an orthonormal set of natural AOs, which are effectively equivalent to the physical orbitals of the atomic wavefunction. Those are strongly separated in maximum-occupancy core and valence orbitals and Rydberg-type orbitals with only negligible occupancies. In the next step, natural hybrid orbitals (NHOs) are generated from the valence orbitals which again are transformed to the two-center bonding and antibonding shared-electron pair orbitals as well as the one-center occupied Lewis lone pairs and unoccupied non-Lewis valence orbitals. Delocalization is described as interactions between Lewis-type (donor) and non-Lewis-type (acceptor) NBOs.^[39]

In Figures 11–13, the compositions of calculated NBOs of the ligand TMGqu and its bischelatate copper complexes are summarized. For the complexes both ligands are described in the same way due to C_2 symmetry and thus one ligand is omitted. The calculations were performed with the NBO 6.0 program^[78] on optimized geometries at B3LYP level of theory with the def2-TZVP and def2-SVP basis sets. For the Cu(II) complex, NBO analysis at def2-TZVP was not performed due

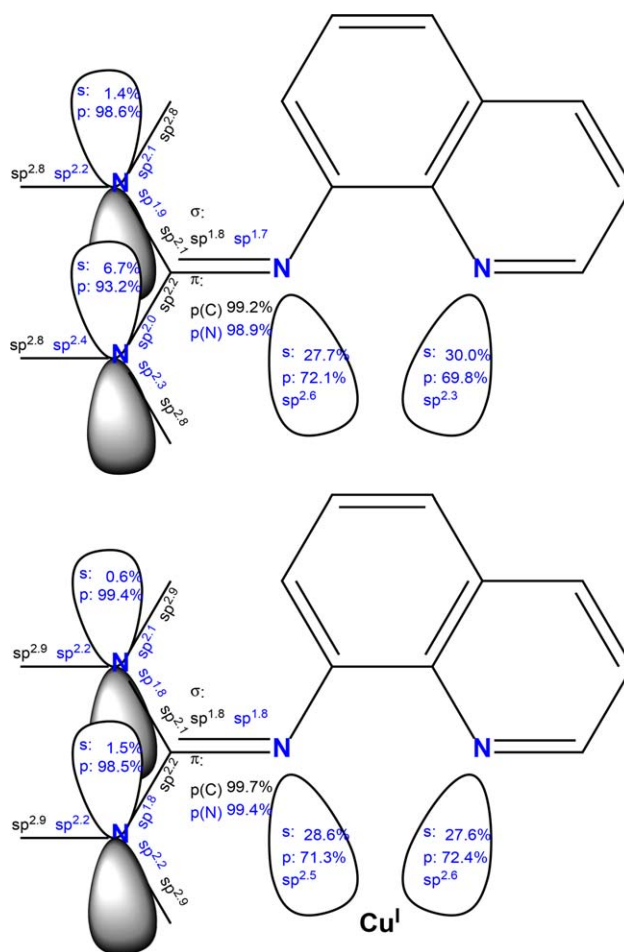


Figure 11. Hybridization of the NBOs for the TMGqu ligand (above) and the Cu(I) complex $[\text{Cu}(\text{TMGqu})_2]^+$ (below) at B3LYP/def2-TZVP level of theory. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

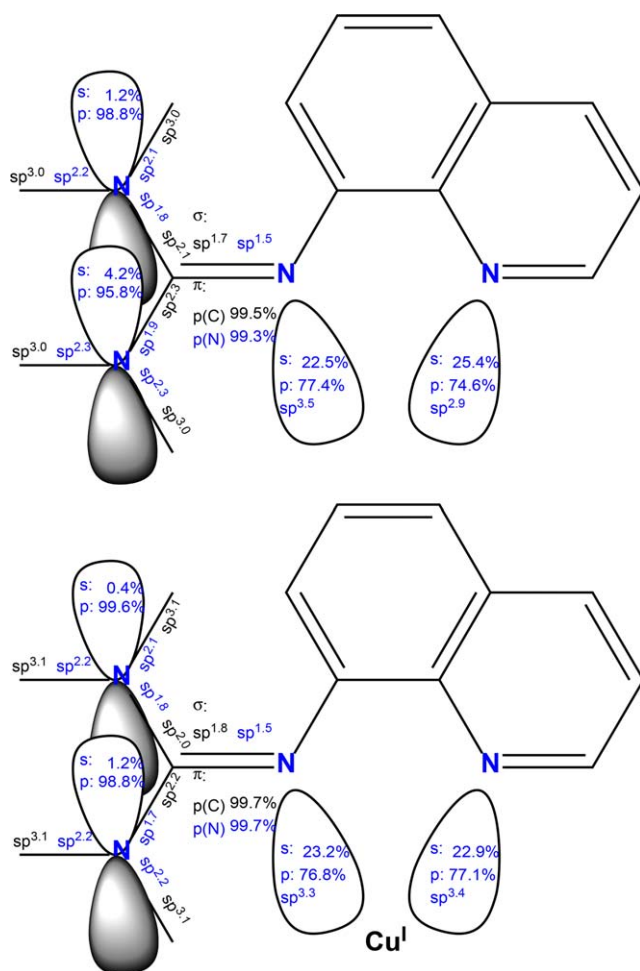


Figure 12. Hybridization of the NBOs for the TMGqu ligand (above) and the Cu(I) complex $[\text{Cu}(\text{TMGu})_2]^+$ (below) at B3LYP/def2-SVP level of theory. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to technical limitations. The comparison of the Cu(I) results for both basis sets (Figs. 11 and 12) shows almost no basis set dependency. For comparative reasons, all calculations were performed with equal resonance Lewis structures with a distinct double bond in the guanidine moiety and lone pairs on the donor N atoms. Possible resonance structures with a N—Cu bond are accounted for with donor–acceptor stabilization energies (Table 5). Due to open-shell calculation of the d^9 Cu(II) complex, the results are shown for both spin orientations (Fig. 13).

The Lewis structures on both donor N atoms and in the guanidine moiety as well as the donor–acceptor interactions have been examined. A sp^2 hybridization is to be expected for

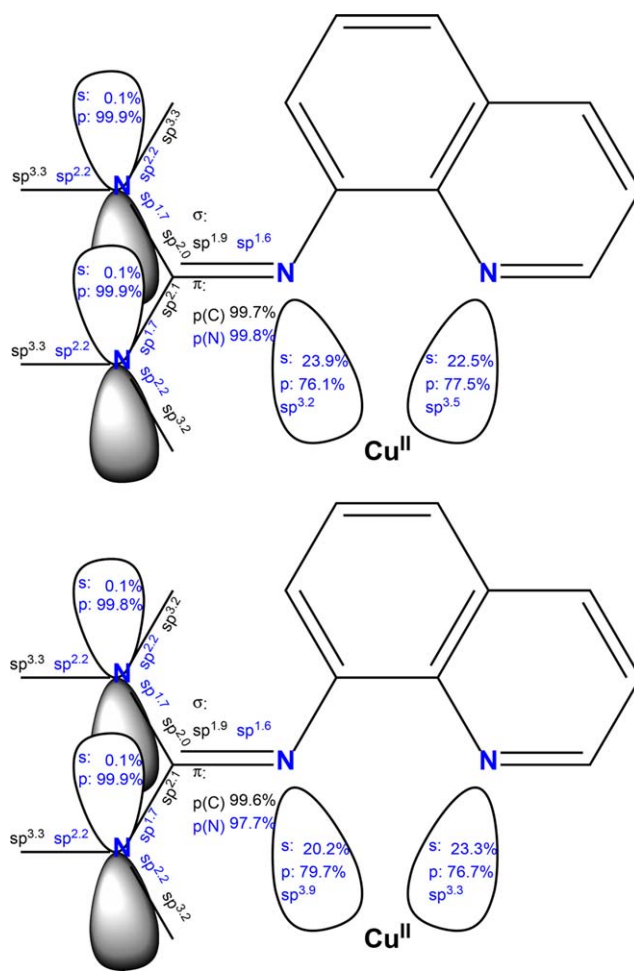


Figure 13. Hybridization of the NBOs for the Cu(II) complex $[\text{Cu}(\text{TMGu})_2]^{2+}$ with α -spin (above) and β -spin (below) population at B3LYP/def2-SVP level of theory. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

all N atoms and the central C atom of the guanidine, whereas the methyl C atoms should be sp^3 hybrids. Further there are lone pairs on all N atoms, with sp^2 hybridization for the donor atoms and with p character on the other N atoms from the guanidine moiety. In Figures 11–13, the compositions of the bonding NBOs and of the lone pairs is shown. Each two-center orbital consists of two one-center NHO.

The hybridizations in the guanidine moiety are as expected and show little basis set dependency. The guanidine lone pairs have a small s character in the free ligand, which is negligible for the Cu(I) complex and nonexistent for the Cu(II) complex. The lone pairs of the donor N atoms show more p character

Table 5. Donor–acceptor stabilisation energies (kcal/mol) for the TMGqu Cu complexes at B3LYP level of theory with different basis sets.

	def2-TZVP Cu(I)	def2-SVP Cu(I)	def2-SVP Cu(II), α -spin	def2-SVP Cu(II), β -spin
$\text{N}_{\text{gua}} \rightarrow \text{Cu} (s)$	19.2	22.2	20.6	16.8
$\text{N}_{\text{gua}} \rightarrow \text{Cu} (d_{x^2-y^2})$	–	–	–	13.4
$\text{N}_{\text{qu}} \rightarrow \text{Cu} (s)$	29.7	30.2	19.6	22.0
$\text{N}_{\text{qu}} \rightarrow \text{Cu} (d_{x^2-y^2})$	–	–	–	12.0

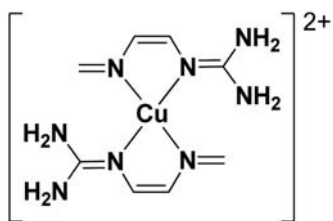


Figure 14. Cu(II) model system.

than in the expected sp^2 hybrid, with $sp^{3.5}$ (N_{gua}), and $sp^{2.9}$ (N_{qu}) hybrids with def2-SVP. The tendency of a larger p character for the donor lone pairs with def2-SVP as opposed to def2-TZVP is also seen for the Cu(I) complex and is the only relevant difference between calculations with these basis sets. In the free ligand, the N_{gua} lone pair has more p character than the N_{qu} lone pair. In the Cu(I) complex, the difference is negligible. For the Cu(II) complex larger differences are observed due to cancellation of the spin degeneration. For the α -spin, the lone pairs show similar composition as for the Cu(I) complex, whereas for the β -spin, the N_{gua} lone pair ($sp^{3.9}$) has a much higher p character than the N_{qu} lone pair ($sp^{3.3}$). The donor-acceptor stabilization energies for the Cu(I) complex amount to 20 kcal/mol for N_{gua} and 30 kcal/mol for N_{qu} . Thus, the quinoline, a relatively soft donor function, is assessed to be a more suitable donor for the soft Cu(I) center as compared to the guanidine. For the Cu(II) complex, the situation is again dependent on the spin. For α -spin, where the only easily available Cu acceptor orbital is the 4 s, the stabilization energies are almost equal (20 kcal/mol) for both donor functions. For β -spin, another unoccupied orbital is available, the $3d_{x^2-y^2}$. The stabilization energies amount to 30 kcal/mol for N_{gua} and 34 kcal/mol for N_{qu} . Thus, both donor functions exhibit equal donor strength for Cu(II).

Cu(II) model system

Similarly as in our previous study on the copper(I) guanidine-imine case,^[23] we performed additional calculations using complementary methodologies for a small bis(chelate) copper(II) model system with two different donors, a guanidine and an imine function to establish error bars for the results predicted here for $[\text{Cu}(\text{TMGu})_2]^{2+}$. The calculations for the Cu(II) model system (cf. Fig. 14) are performed using a plane-wave (pw) basis set as well as a def2-TZVP basis.

The molecular structures predicted on the basis of B3LYP and PW91 calculations for $[\text{Cu}(\text{TMGu})_2]^{2+}$ are very similar, as shown in Table 6. The largest deviation of about 0.02 Å is found for the Cu– N_{gua} bond lengths, where B3LYP results in slightly longer bonds. An opposite behavior is found for the C–N bonds of the guanidine moiety that are nearly 0.01 Å longer when using PW91. The same trend holds for the structure of the Cu(II) model system, where PW91 yields as well shorter Cu–N bonds and longer C–N bonds, but provides overall a structure very similar to the one obtained from the B3LYP calculations. The most striking difference caused by modifying the XC functional concerns the angle between the chelate planes, which is clearly larger using local rather than

hybrid functionals. The structure of the first coordination sphere of the Cu(II) model system closely resembles that of GQ Cu(II). The Cu–N bond length to the guanidine changes marginally, and the delocalization of the C=N double bond of the guanidine moiety is very high for both complexes as seen in the almost equal C–N bond lengths. The Cu–N imine bond is slightly larger than the quinoline bond in the larger GQ Cu(II) system, which is expected from the better N donor properties of the quinoline. A remarkable influence of the basis set is observed for both complexes: The Cu–N bonds are about 0.01–0.02 Å shorter and C– N_{amine} bonds are up to 0.05 Å longer when the electronic orbitals are expanded into plane waves. Comparing GQ Cu(II) and Cu(II) model system calculations based on the PW91 functional show a 1.5% (B3LYP 1.0%) Cu– N_{qu} bond contraction for the latter as the most pronounced difference. This corresponds to an absolute difference of –0.031 Å (B3LYP –0.020 Å). Plane-wave calculations based on PW91 corroborate the trend found with the def2-TZVP basis concerning the geometry of the Cu coordinating nitrogen atoms. Application of dispersion with Becke–Johnson damping for both systems shows a significant bond contraction (small: guanidine: –0.016 Å, imine: –0.012 Å; GQ: guanidine: –0.029 Å, qu: –0.017 Å), whereby the guanidine bond is more shortened. In fact, this effect is more pronounced in the GQ complex as here, the steric repulsion becomes important. In summary, we find that (i) the Cu(II) model system reproduces essentially the atomic distances that characterize the Cu(II) coordination in GQ Cu(II) and (ii) that the geometrical details depend as strongly on the basis set as they depend on the XC functional: calculations with a complete set of basis functions yield in particular shorter Cu–N bonds. However, the angle between the chelate planes is strongly disturbed by the simplification to the small model.

Next, we turn to excitation properties and study the electronic structure and optical response of the Cu(II) model system. Similar to GQ Cu(II) discussed earlier, we find the TD-DFT spectra to depend strongly on the XC functional. In particular, the local PW91 gives rise to far smaller excitation energies than the hybrid functional B3LYP. Also line shape and peak intensity are modified. The absence of the quinoline moiety causes some differences between the optical response of GQ Cu(II) and the Cu(II) model system. This can be understood from the frontier molecular orbitals of the two systems. As seen in Figure 15, the model system lacks the π orbitals of the quinoline, which provide an essential contribution to GQ Cu(II) frontier MOs and are involved strongly in the charge-transfer transitions. In case of the model system Cu d-type orbitals are very prominent among the frontier orbitals. With B3LYP, the β -spin LUMO is located between the occupied and the unoccupied ligand-type orbitals and the α -spin SOMO as well as other Cu d orbitals are stabilized and relatively low in energy. The same behavior is found for GQ Cu(II). With PW91, the β -spin LUMO is slightly stabilized and consequently, the SOMO and other Cu d orbitals are destabilized.

In Figure 16, it can be seen that in the energy region around the HOMO and LUMO orbitals the molecular orbital spectra of GQ Cu(II) and Cu(II) model system are similar and

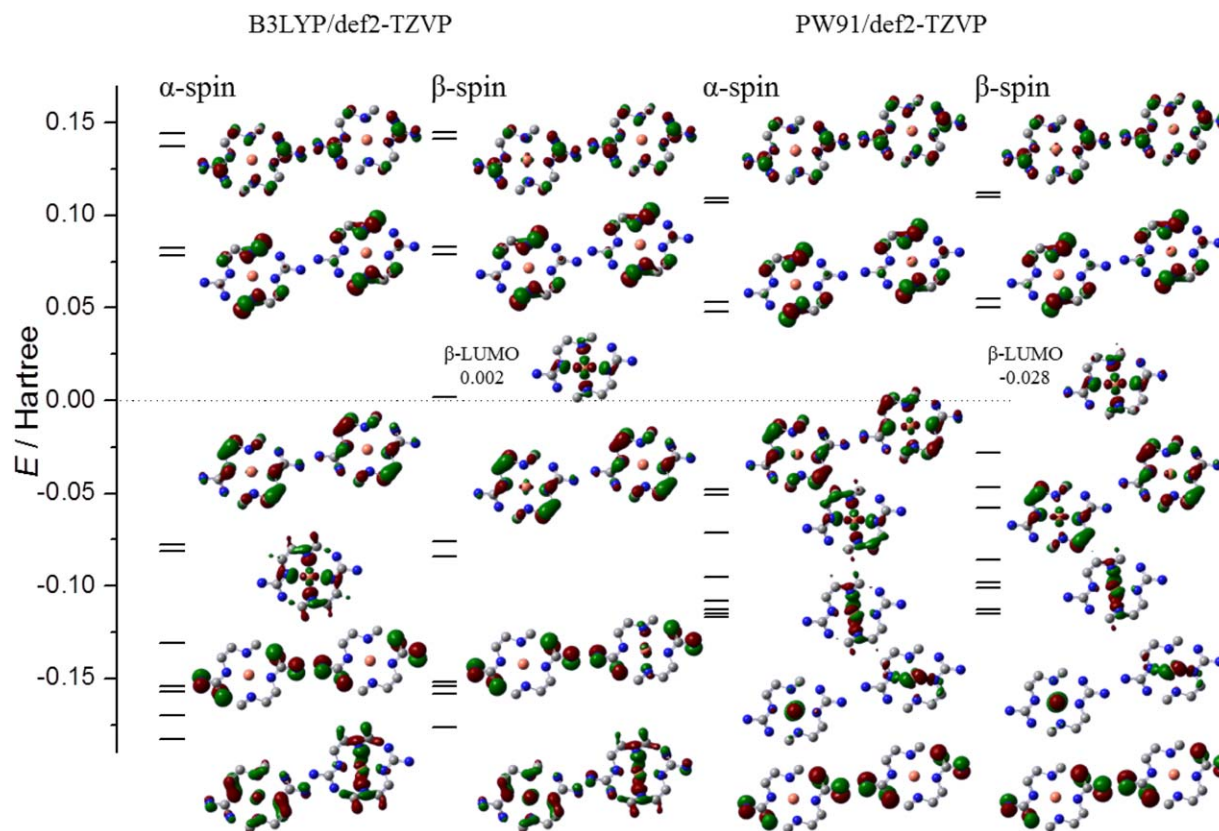
Table 6. Selected bond lengths (Å) and angles (°) for calculated structures of the $[\text{Cu}(\text{TMGqu})_2]^{2+}$ cation and the Cu(II) model system for various XC functionals and basis sets.

Cu(II)	Method	Cu—N _{gua}	Cu—N _{qu}	C=N _{gua}	C—N _{amine}	Angle betw. chelate planes CuN ₂ —CuN ₂	
Model	B3LYP/def2-TZVP	2.017	2.035	1.339	1.339	1.341	51.8
Model	B3LYP/def2-TZVP-BJ	2.001	2.023	1.337	1.338	1.340	48.2
Model	PW91/def2-TZVP	2.010	2.028	1.351	1.343	1.343	57.9
Model	B3LYP/pw	1.998	2.022	1.337	1.341	1.341	56.5
Model	PW91/pw	1.989	2.014	1.350	1.381	1.392	60.1
GQ	B3LYP/def2-TZVP	2.018	2.015	1.350	1.349	1.354	49.9
GQ	B3LYP/def2-TZVP-BJ	1.989	1.998	1.343	1.351	1.347	46.7
GQ	PW91/def2-TZVP	2.017	1.997	1.356	1.355	1.362	52.5
GQ	B3LYP/pw	2.007	2.013	1.349	1.355	1.350	51.0
GQ	PW91/pw	2.006	1.983	1.356	1.370	1.401	53.3

show nearly a one to one correspondence of the states. Above and below this region the additional orbitals and their interaction leads to noticeable differences between the two system. This carries over the optical excitations, as can be seen from the IPA spectra shown in Figure 17: while the excitations are similar in energy position and line shape at the absorption onset, marked differences occur for larger excitation energies. This means that the electronic and optical excitations of the Cu(II) model system discussed below have to be transferred with care to the larger GQ Cu(II) complex.

In Figure 18, the molecular orbital spectra of the Cu(II) model system obtained within DFT using local and hybrid functionals based on a def2-TZVP basis as well as plane waves

is compared with QP calculations within the GW approximation. Thereby, the influence of the self-consistency is probed by iterating twice the single-particle Greens function (G_0W_0 vs. G_2W_0). Calculations utilizing different basis sets show only very small differences for the occupied spin orbitals. However, as expected, larger deviations occur in the unoccupied states. With increasing energy the electron orbitals tend to be less and less localized and are, thus, much better described by a plane-wave basis than by a limited number of localized basis functions. As shown in Figure 18, the density of electron states above the LUMO is markedly higher for the pw klein oder groβ calculations compared to the def2-TZVP basis, irrespective of the XC functional. Concerning the occupied states, the

**Figure 15.** Frontier orbitals of the Cu(II) model system at B3LYP and PW91 levels of theory (detailed orbital view of Fig. 16). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

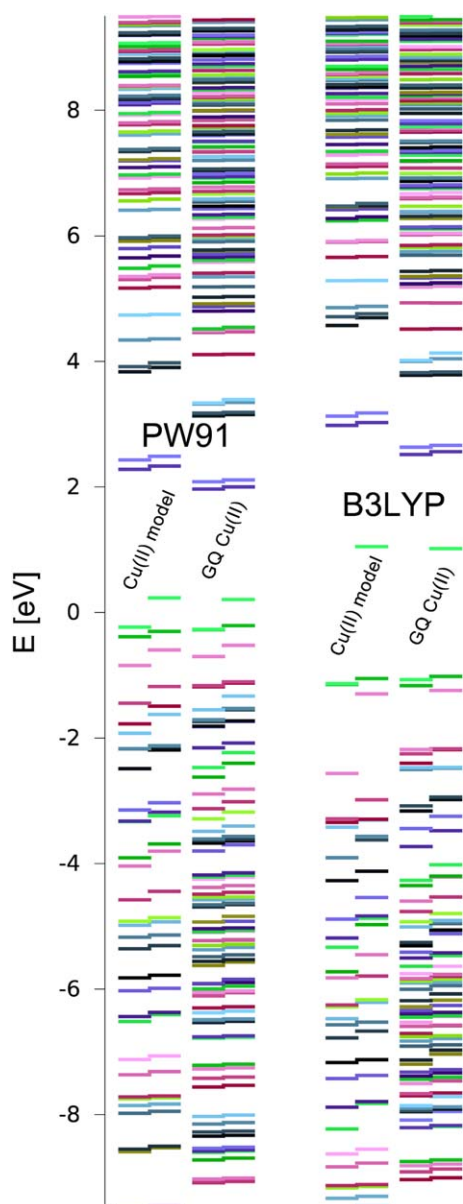


Figure 16. Kohn-Sham (KS) molecular spin-orbital spectra of the Cu(II) model system in comparison to GQ Cu(II). The colors are used to indicate states of similar orbital character. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

HOMO and HOMO-1 orbitals of the α -spin channel are also influenced by the choice of the basis set (including also structural relaxation effects). In particular, we observe that the lowest energy transition occurs between α and β -spin states in pw calculations using PW91, whereas it occurs in the same spin channel if the calculations are performed with localized basis function. However, the energy shifts due to basis set changes if compared to the self-energy shifts obtained from QP calculations in the GW approximation. The latter lead to strong and state-dependent shifts that in case of an electronic start configuration obtained within PW91 inverts the energy order of the HOMO states in the two spin channels. Such a reordering does not occur if the calculations are based on an electronic structure obtained from B3LYP. QP shifts, however, lead to a reorder-

ing of some unoccupied electronic states irrespective of the XC functional used to generate the start wave functions. They also widen the HOMO-LUMO gap substantially: we calculate a HOMO-LUMO gap of 0.46 eV for the DFT PW91 calculations (2.1 eV B3LYP). GW calculations open the gap to 3.63 and 4.85 eV for PW91 and B3LYP, respectively. Including two additional iterations of the Greens function lead to nearly converged QP energies with a QP gap of 4.29 and 5.58 eV for PW91 and B3LYP start electronic structures, respectively.

In Figure 19, we compare various theoretical approaches to the Cu(II) model system optical response. Thereby, we focus on calculations that start from the B3LYP electronic structure. Using PW91 as starting point for the calculations leads to similar features that occur, however, at lower excitation energies. Surprisingly, TD-DFT and IPA yield optical spectra that are comparable with respect both to the excitation energies and the line shape. This indicates that electron self-energy effects are nearly offset by the electron-hole attraction in the small molecule and suggests the IPA as an inexpensive yet reliable approach to its optical excitations. Very much in contrast to the good agreement between TD-DFT and IPA, it is found that G_0W_0 +BSE calculations in Tamm-Dancoff approximation (TDA) result in far too low absorption energies and show no resemblance to the TD-DFT spectrum. The comparison is slightly improved if one goes beyond the TDA and includes the resonant-nonresonant coupling terms. This blue shifts the spectrum by about 1 eV. An additional blueshift of similar magnitude is obtained if selfconsistency effects are included in the Greens function. The resulting G_2W_0 +BSE spectrum resembles the TD-DFT results for excitations above around 3 eV. However, it features a very pronounced low-energy excitation at about 0.7 eV, which has essentially no counterpart in either the TD-DFT or the IPA spectrum. The onset of the TD-DFT as well as of the IPA spectrum is given by an optical transition

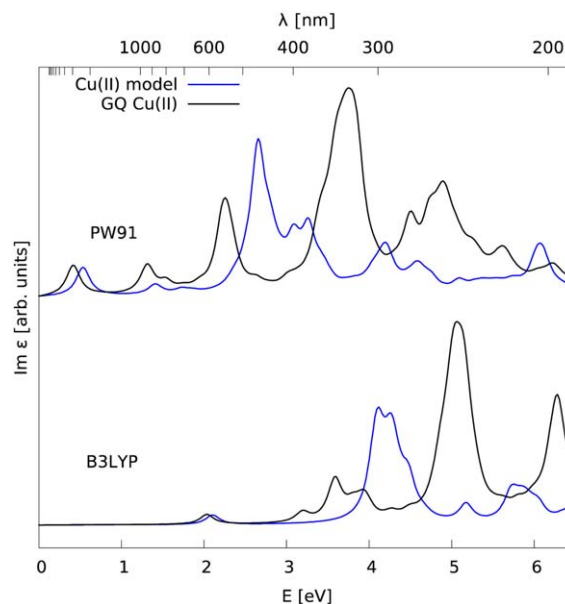


Figure 17. Comparison of IPA spectra from small and large Cu(II) system. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

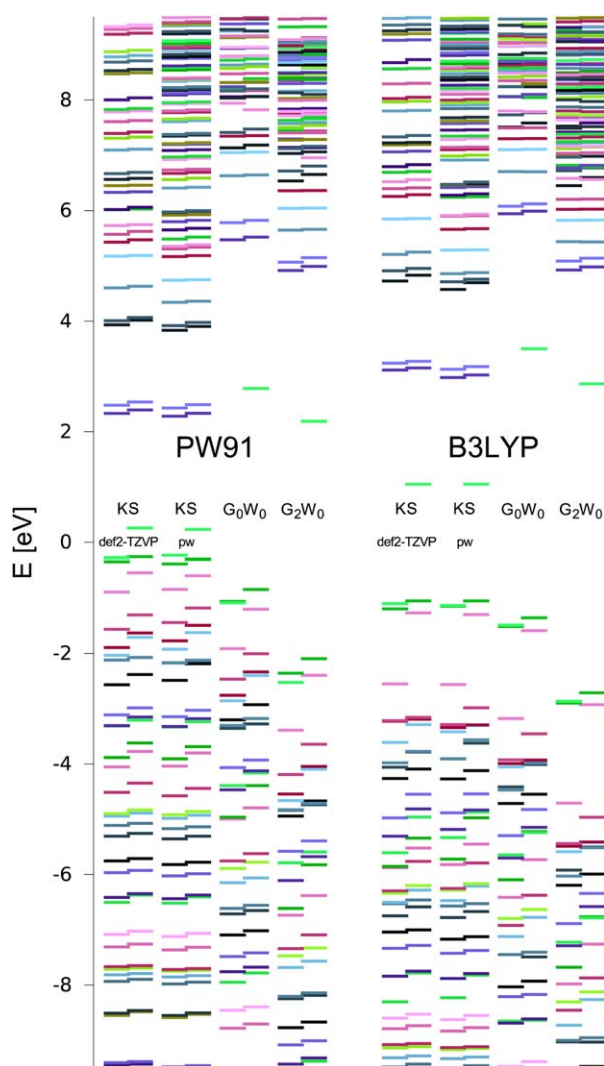


Figure 18. Kohn–Sham (KS) and GW molecular spin-orbital spectra of the Cu(II) model system. The colors are used to indicate states of similar orbital character. This coding is strictly valid only within the same functional. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that mainly involves the respective HOMO and LUMO states but has a very low oscillator strength (see inset in Fig. 19). The analysis of the origin of the first, pronounced peak resulting from the solution of the BSE, however, shows that it cannot be explained in terms of single-particle HOMO–LUMO transitions. There are reports of occasional spurious excitations calculated using either TD-DFT or MBPT, see, for example, Refs. [72,79]. The system studied here can be expected to be particularly prone to such artifacts, due to the involvement of strongly localized Cu d electrons with strong electron correlation and self-interaction effects. To clarify the situation, we performed additional Δ SCF calculations for the lowest optical absorption energy and the corresponding transition matrix element. If applied to the lowest excitation energy, Δ SCF is a conceptually simple and elegant way to account for electronic relaxation effects. The results are shown in the inset in Figure 19. The calculations lead to a Δ SCF excitation energy of 2.2 eV. The orbital character of the corresponding excitation resembles the

one of the TD-DFT excitation at about 1 eV and the (second) G_2W_0 + BSE peak at around 2.3 eV. This holds also for the oscillator strength. The oscillator strength assigned to the Δ SCF transition has been approximated by both using the unrelaxed and the relaxed electron wave functions in the matrix element calculation. Both approaches give rise to similar values. TD-DFT as well as Δ SCF thus support the picture obtained from the IPA, which also predicts a HOMO–LUMO related transition of weak oscillator strength as absorption onset. The spurious first absorption peak predicted within G_2W_0 + BSE, however, is most likely an artefact of the static Bethe–Salpeter kernel that uses a screening model derived for the comparatively homogenous charge distribution in semiconductors.^[68,80] Altogether, the present calculations suggest both TD-DFT as well as IPA as reliable tools for optical response calculations for the Cu(II) model system.

Finally, we conclude that B3LYP seems to serve as a good starting point for the electronic structure calculations of the present charge-transfer systems which are of considerable size. In the literature, B3LYP is discussed ambiguously: on the one hand, this “workhorse” of quantum chemistry yields astonishingly good energetic and optical predictions with small basis

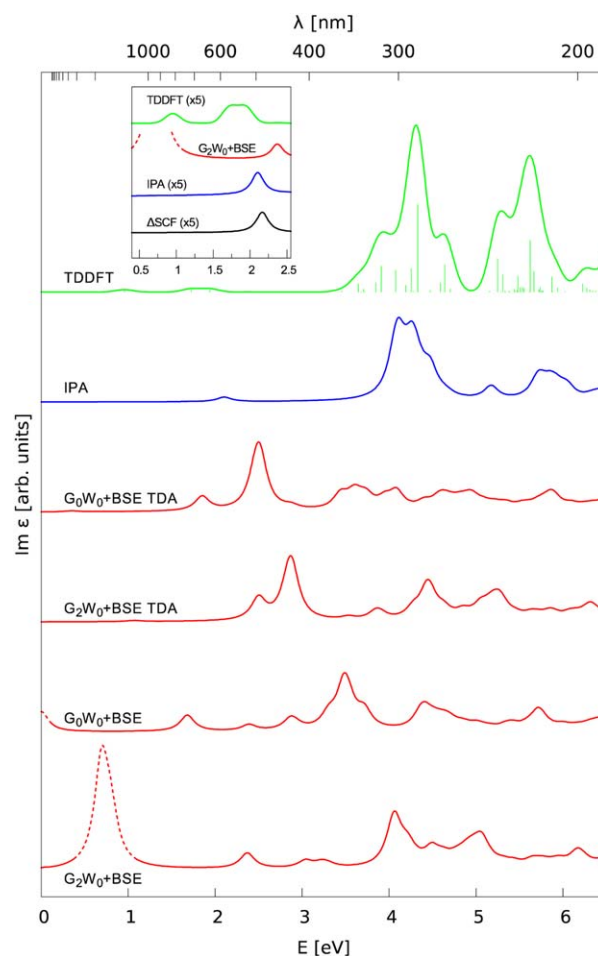


Figure 19. Comparison of absorption spectra calculated with TDDFT, IPA, MBPT (GW + BSE) as well as Δ SCF for the Cu(II) model system. The spectra are based on an electronic structure obtained within B3LYP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

sets and is hence extremely widely used^[81–86]; on the other hand, it suffers from severe shortcomings such as increasing energetic errors with increasing molecular size and sometimes unreliability for transition metal systems.^[81] Ramos et al. found that B3LYP is an average performing functional for small copper complexes. Interestingly, they did not detect an influence of the use of dispersion D3, possibly due to the small size of the regarded complexes.^[84] Although future calculations probably will be based more and more on double-hybrid functionals such as B2PLYP, at present their high computational costs are hindering their routine application.^[81] Conversely, the comparatively recent TPSSh functional seems to provide a viable option for large systems.^[81,85] With regard to structural and optical description presented here, this seemingly holds also for charge-transfer systems.

Conclusion

In summary, our results indicate a strong influence of the exchange and correlation functional on the structural properties of copper(II) guanidine–quinoline complexes. In addition, calculations performed with a plane-wave basis show that the influence of the basis set on the structural details of the molecular complexes studied here is of similar magnitude as the one due to various XC functionals. The structural benchmarking indicates that B3LYP/def2-TZVP and TPSSh/def2-TZVP offer both reasonable structural descriptions (predictions within the error bars of the experimental structures) but that the addition of dispersion with Becke–Johnson damping offers best structural agreement for extremely low computational costs. Here, we found that especially the DFT-D3 approach with Becke–Johnson damping yields better results than earlier versions of dispersion correction. The def2-TZVP basis set has proven to offer a structural convergence for the regarded systems. With def2-TZVP and Becke–Johnson damping, the functionals B3LYP and TPSSh give the accuracy of crystallographically determined structures (error: 0.012 Å, 0.5% of bond lengths).

Concerning the optical response calculations, it is found from IPA and Δ SCF calculations that adiabatic linear-response TD-DFT is a viable approach to copper(II) charge-transfer systems while the Bethe–Salpeter approach, at least using a static kernel with a simplified screening, may give rise to spurious excitations. In any event, a realistic description of the molecular optical response within MBPT requires the inclusion of the resonant–nonresonant coupling terms in the exciton Hamiltonian as well as selfconsistency effects in the Greens functions. The TD-DFT optical benchmarking demonstrates that B3LYP/def2-TZVP calculations model well the experimental data (error <0.1 eV) with little influence of the description of dispersion interaction and that the Becke–Johnson damping does not change this picture. The canonical MOs are heavily mixed and the NTO analysis gives only some simplifications. LMCT transitions are present throughout the spectrum. This challenge is tackled astonishingly well by the hybrid functionals B3LYP and TPSSh. More astonishingly, we found that the structural and optical solvent influence for Cu(I) and Cu(II) is rather marginal. The NBO analysis for the TMGqu ligand and its Cu(I) and Cu(II)

complexes reveals the importance of the guanidine donors and their internal stabilization through the CN₃ moiety.

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Keywords: copper • TD-DFT • many-body perturbation theory • ligand-to-metal charge-transfer • guanidine

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Supporting Information

Geometrical and optical benchmarking of copper(II) guanidine-quinoline complexes: Insights from TD-DFT and many-body perturbation theory (Part II)

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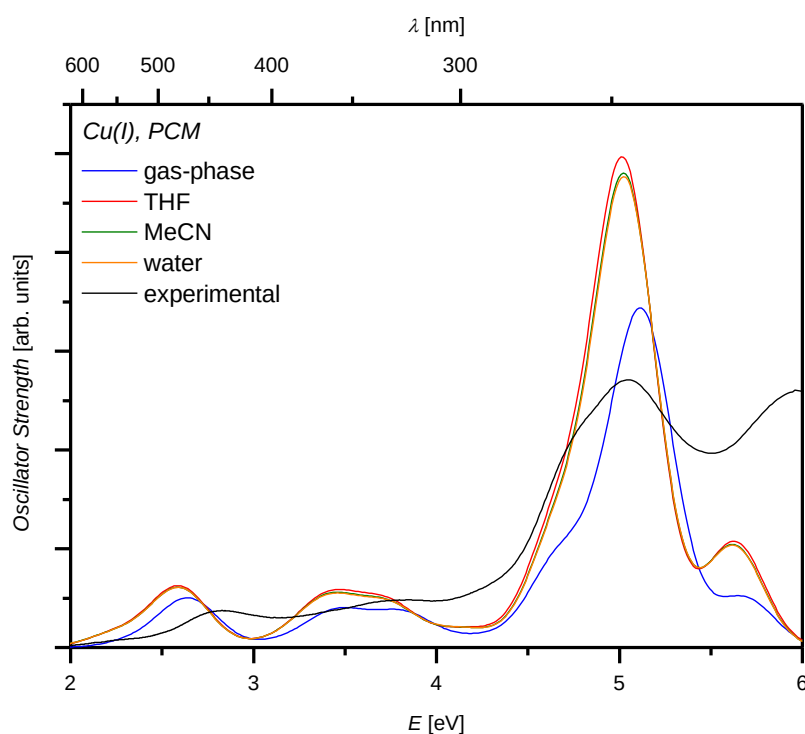


Figure S1. TD spectra for the $[\text{Cu}(\text{TMGu})_2]^+$ cation with the IEF-PCM solvation model and different solvents

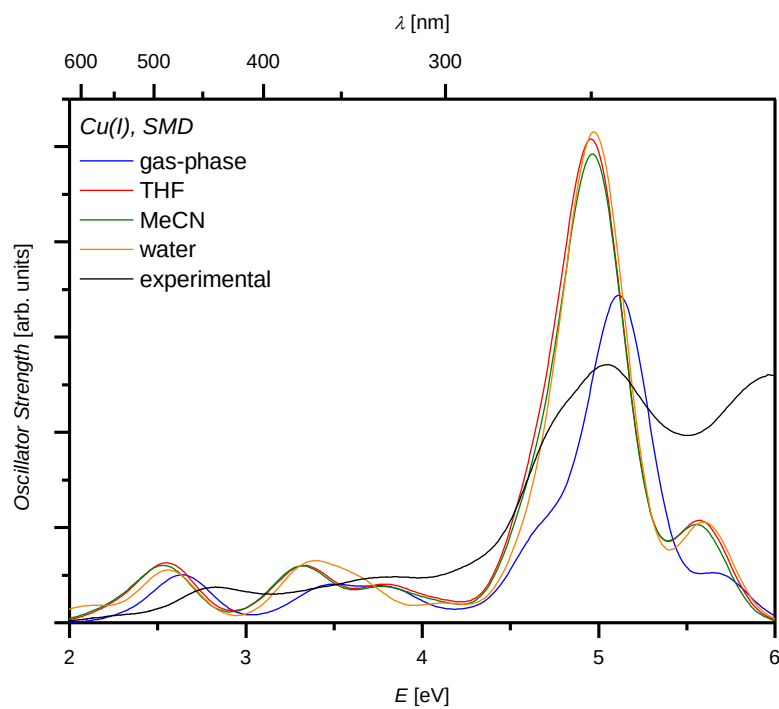


Figure S2. TD spectra for the $[\text{Cu}(\text{TMGu})_2]^+$ cation with the SMD solvation model and different solvents.

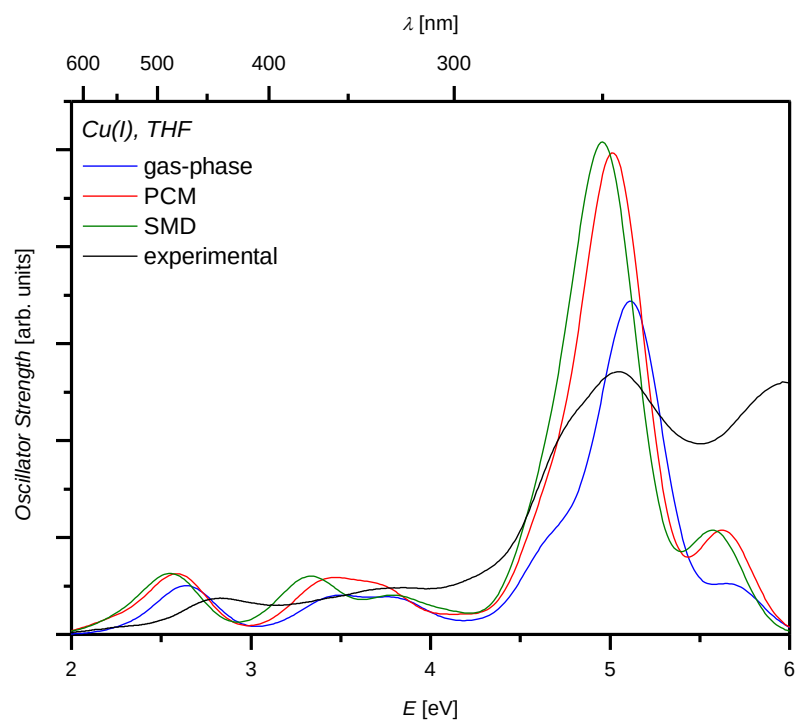


Figure S3. TD spectra for the $[\text{Cu}(\text{TMGu})_2]^+$ cation with the SMD and PCM solvation model with THF as solvent.

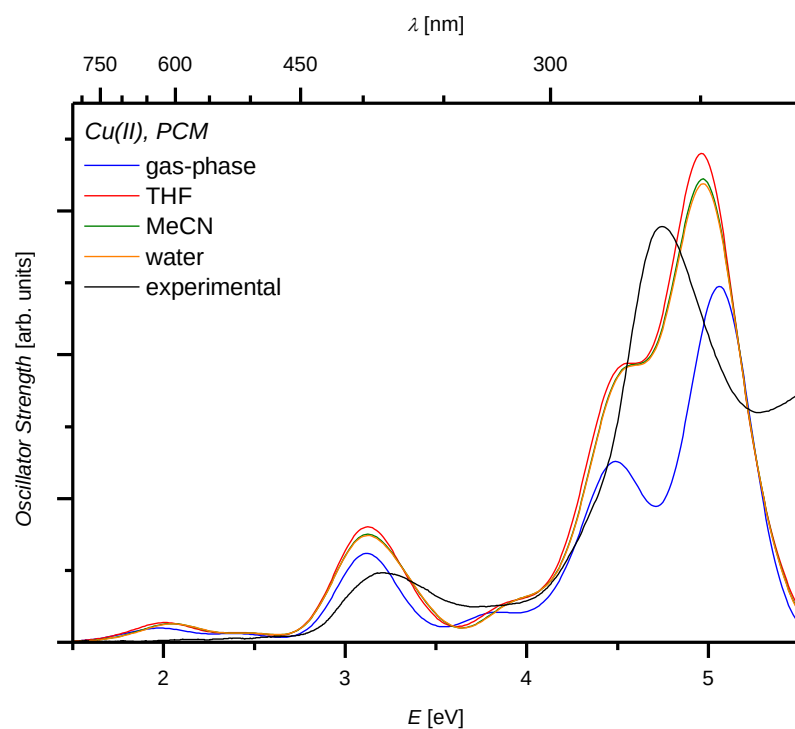


Figure S4. TD spectra for the $[\text{Cu}(\text{TMGu})_2]^{2+}$ cation with the IEF-PCM solvation model and different solvents.

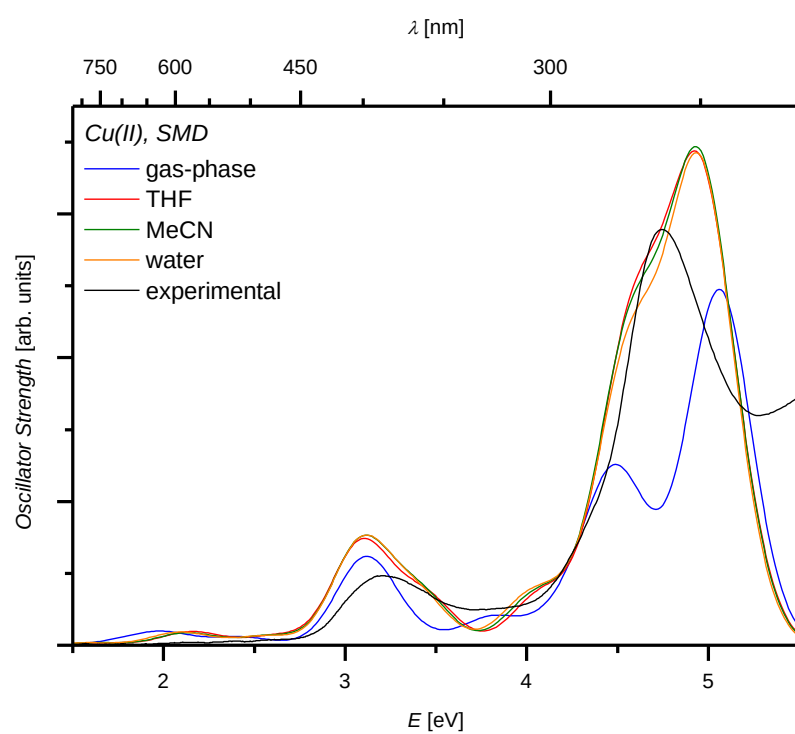


Figure S5. TD spectra for the $[\text{Cu}(\text{TMGu})_2]^{2+}$ cation with the SMD solvation model and different solvents.

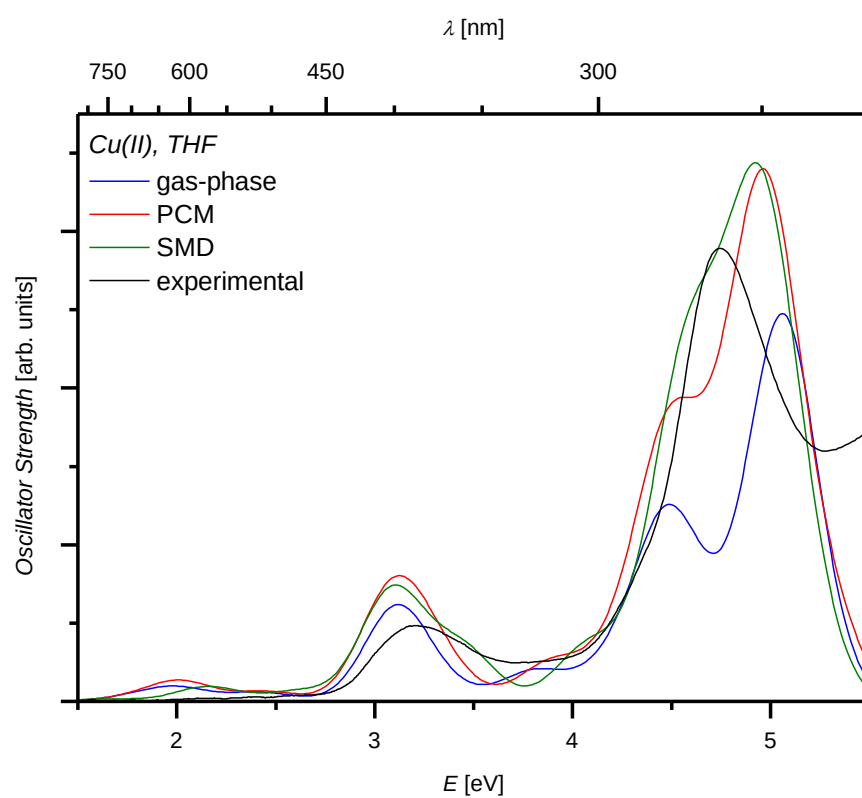


Figure S6. TD spectra for the $[\text{Cu}(\text{TMGu})_2]^{2+}$ cation with the SMD and PCM solvation model with THF as solvent.