Quantum chemical study of the electronic properties of an Iridium-based photosensitizer bound to medium-sized silver clusters

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A B S T R A C T

The equilibrium structures and electronic excitation spectra of the Ir(III) photosensitizer [Ir(ppy)$_2$(bpy)]$^+$ bound to medium-sized silver clusters Ag$_n$ ($n = 19, 20$) are investigated using time-dependent density functional theory. The long-range corrected LC-BLYP approach is used with a system-specific range separation parameter. The weak physisorption of the hybrid complexes yields only small changes in the broadened absorption spectra of the hybrid system as compared with its constituents. However, the density of states as well as the fine structure of the spectra is strongly modified upon complexation. It is shown that the standard range separation parameter (0.47 bohr^{-1}) cannot predict these properties correctly and the optimized value of 0.16 bohr^{-1} should be used instead.

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1. Introduction

The combination of metal nanoparticles or nanowires with various organic adsorbates such as dyes, peptides, and J-aggregates is an active area of research with applications in bio-sensing, catalysis, and medicine [1–5]. Numerous theoretical and experimental studies of nanoparticle-organic hybrid systems have been reported (for reviews, see, e.g., Refs. [6–9]). These hybrid systems exhibits new composition dependent properties, which differ from those of the separate constituents This includes the enhancement or quenching of fluorescence, absorption, and Raman scattering due to surface and plasmon resonances, the broadening of the absorption range to yield an antenna effect, and modified "redox" properties, see, e.g., Refs. [10–14].

In the present communication we discuss results on the electronic properties of a model system comprised of the [Ir(ppy)$_2$(bpy)]$^+$ photosensitizer (IrPS) shown in Fig. 1, bound to medium-sized silver clusters Ag$_n$ (n = 19, 20). Our choice of the system is motivated by the use of heteroleptic Ir(III) complexes as photosensitizers in a photocatalytic system for water splitting introduced by Beller et al. [15]. The original homogeneous system includes triethylamine as a sacrificial reductant and a series of iron carbonyls as water reduction catalysts. The absorption spectrum of the IrPS overlaps with the sun's spectrum only in its long wave

length tail between 300 and 450 nm [16]. Therefore, extending the range of absorption further into the visible by coupling the IrPS to silver nanoparticles might provide a means to enhance the overall efficiency of this photocatalytic system.

Because of size of the systems under study, density functional theory (DFT) [17] and its extension into the time-dependent (TD) domain in the linear response limit [18] is the natural choice for studying ground and excited state properties. However, the correct description of long-range charge-transfer (CT) properties, which is mandatory for hybrid systems, can not be achieved applying conventional DFT functionals [19–23]. By introducing exact Hartree–Fock exchange in long-range correction schemes like LC-BLYP a correct asymptotic behavior and a more balanced description for CT states is obtained. In our previous study on bare IrPS [16], the LC-BLYP approach [24–26] was shown to give excitation energies in good agreement with experimental data and results of CASSCF/CASPT2 calculations.

The binding of IrPS to small silver clusters (one to six silver atoms) has been studied in Ref. [27] using the LC-BLYP approach. Already for this size of the hybrid system pronounced changes in the electronic absorption spectrum had been observed. Moreover, the electronic properties were found to be rather sensitive to the number of silver atoms. For instance, binding energies and localization of HOMO and LUMO orbitals oscillate with the number of silver atoms in an even/odd like fashion. Whether such a behavior propagates to larger clusters and how it influences the photophysical properties is the topic of the present study. A detailed understanding of excited state properties of larger cluster-dye hybrid

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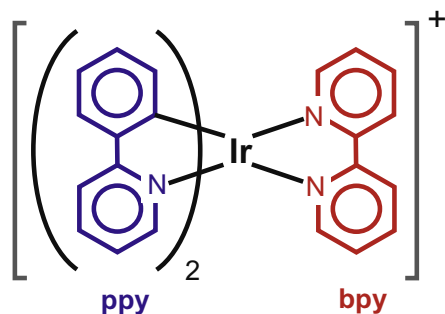
Fig. 1. Chemical formula of the photosensitizer [Ir(ppy)$_2$(bpy)]$^+$ (IrPS).

systems shall be valuable for the characterization of systems composed, for instance, of size-selected clusters interacting with dye molecules at surfaces.

The paper is organized as follows. In Section 2 we give the computational details putting emphasis on the tuning of the range-separation functional in LC-BLYP. The results are presented in Section 3, including electronic ground state structures and electronic absorption spectra. A summary is provided in Section 4.

2. Computational details

In the long-range separation approach, LC-BLYP, a parameter ω is introduced, which defines the separation of the Coulomb operator into long-range and short-range parts, with the long-range part then being described by the exact exchange integral. In a number of publications, it has been demonstrated that an appropriate tuning of ω leads to a significant improvement of fundamental and optical gaps, CT and Rydberg excitation energies as well as ionization potentials (IPs) [28–31]. A systematic procedure for the determination of an optimal ω has been suggested in Refs. [32–34]. It is based on finding that ω, which minimizes the following functional

$$J(\omega) = J_N(\omega) + J_{N+1}(\omega)$$
$$= \left| \varepsilon_{HOMO}^{\omega}(N) + IP^{\omega}(N) \right| + \left| \varepsilon_{HOMO}^{\omega}(N+1) + IP^{\omega}(N+1) \right|. \quad (1)$$

In other words, the optimized ω will provide a compromise for fulfilling Koopmans' theorem simultaneously for systems with N (cation complex) and $N + 1$ (neutral complex) electrons. In Eq. (1), $\varepsilon_{HOMO}^{\omega}$ and IP^{ω} is the HOMO energy and the IP, respectively.

In Refs. [23,35–37], we have applied optimal tuning to study charge transfer in a particular photocatalytical system for water splitting [15]. We have shown that the LC-BLYP functional with optimally-tuned range-separation parameter provides good agreement with experiments for IrPS in oxidized and reduced forms [35]. It was also successfully applied to the explanation of experimental findings on luminescence quenching in IrPS-TEA [36] and IrPS-Fe-cat systems and relative catalytic activity in a row of iron carbonyls [37]. This justifies the present application of this approach to IrPS–Ag$_n$ to predict, e.g., electronic absorption spectra for which experimental data are still missing. All methodological issues regarding the tuning of the range-separation parameter are presented in Ref. [35] including hybrid systems such as IrPS–Ag$_n$ (n = 2, 10, 20).

Here, we give a more detailed account on the case of IrPS–Ag$_{10}$. In short, the IPs and HOMO energies of neutral species, anions, and cations have been obtained from single-point energy calculations at the optimized geometry of the electronic ground state. Similar to the small systems [27], the geometry optimization was carried out without symmetry constraints. Initial geometries of IrPS for further optimization were taken from Ref. [16] (assuming C$_2$ point symmetry [38]). The initial structures of Ag$_{10}$ were taken from Ref.

[39], those of Ag$_{19}$ and Ag$_{20}$ from Ref. [40], except tetrahedral Ag$_{20}$ which had been studied before in Refs. [41–43]. Binding energies have been obtained including the counterpoise method to correct for the basis set superposition error (BSSE) [44,45].

Vertical excitation spectra have been calculated by means of the TDDFT approach. The number of included transitions has been 450 and 650 for XXa and IXXo, respectively (for structures abbreviations, see Fig. 3 and Section 3.2). A Lorentzian broadening (0.4 eV) has been added to the stick-spectra. Spin-forbidden transitions have not been included in the present TDDFT investigation despite high spin–orbit coupling constant of Ir. As shown in recent studies on the influence of spin–orbit coupling on the absorption spectra of similar Ir metal–organic complexes, singlet/triplet mixing reflects itself in a small red shift of the visible domain and a decrease of intensities as triplet states possess low oscillator strengths. In general, the influence is only minor, especially for those states that are localized on the ligands what justifies to neglect spin–orbit coupling in a first approximation [46–49].

All calculations were performed with the Gaussian09 program package [50] using the LANL2DZ effective core potential basis set for Ir and Ag and the 6–31G(d) basis for all other atoms.

3. Results and discussion

3.1. Range-separation parameter optimization

In Fig. 2, the procedure for tuning ω is demonstrated for the case of IrPS–Ag$_{10}$. A minimum of $J(\omega)$ at 0.16 bohr^{-1} has been found. Around 0.63 bohr^{-1} an additional higher energetic minimum occurs. This can be traced to the change of the character of the lowest adiabatic state of the cationic species, where the order of HOMO and HOMO-1 orbitals are interchanged. Here, the unpaired electron initially localized on the π^*(bpy) orbital of the reduced doublet IrPS is transferred to the σ(Ag$_{10}$) orbital [51].

The obtained optimal ω value is substantially smaller than values of 0.33 bohr^{-1} and 0.47 bohr^{-1} (shown as vertical lines in Fig. 2) implemented in common quantum chemical packages. This is not surprising since these (standard) values were determined for test sets of diatomics and small molecules [25,52].

Since the inverse of ω reflects a characteristic distance for switching between short- and long-range parts of the exchange contribution, optimal ω values were shown to decrease with increasing system size and conjugation length [28,29,31,34,53–56]. This size-dependence, however, is not monotonous and there is a strong
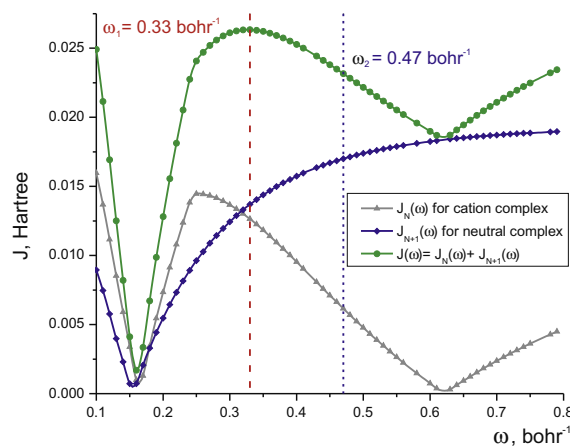

Fig. 2. Optimization of range-separation parameter for the case of IrPS–Ag$_{10}$. The functions $J_N(\omega)$ and $J_{N+1}(\omega)$ are defined in Eq. (1) and represent the conditions for fulfilling Koopmans' theorem for the cationic and neutral species, respectively.