

Chapter2

Investigated Materials and Methods

In this chapter the dyes used in my experiment are described. Then the physical and (electro)chemical properties of well-known chromophores used generally in dye solar cells is compared to metal-free dye compound.

2.1 Chromophores

The efficiencies of the sensitizers used in dye-sensitized solar cells (DSSCs) are related to some basic criteria [1]. The highest occupied molecular orbital (HOMO) energy potential of the dye should be sufficiently positive with respect to the HTM/electrolyte redox potential for efficient dye regeneration [2]. On the other hand, the lowest unoccupied molecular orbital (LUMO) energy potential of the dye should be sufficiently negative to match the potential of the conduction band edge of the TiO₂. It is also worth to mention that the light absorption in the visible region should be efficient [3].

However, by broadening the absorption spectra the difference in the energy levels of the HOMO and the LUMO is decreased. If the HOMO and LUMO energy levels are too close in potential, the driving force for electron

injection into the semiconductor or regeneration of the dye from the electrolyte could be hindered. The sensitizer should also exhibit small reorganization energy for excited and ground-state redox processes, in order to minimize free energy losses in primary and secondary electron transfer steps.

2.1.1 Classical chromophores

(a) Ruthenium Based Chromophores

Chromophores of ruthenium complexes such as the N3/N719 [4] dyes and the black dye [5] have been intensively investigated and showed record solar energy-to electricity conversion efficiencies (η) of 11% (Figure 2.1).

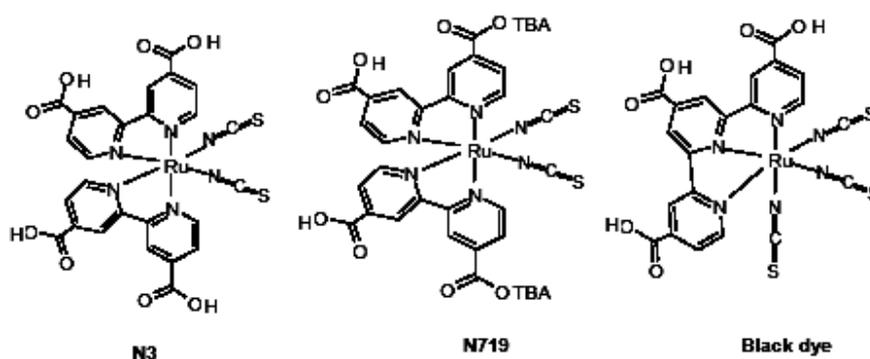


Figure 2.1 The chemical structures of the Ruthenium based sensitizers.

A large number of ruthenium based sensitizers have been investigated in order to improve the photovoltaic performance and the stability of the DSSCs [6-9]. Recently, K19 and K77 attract more attention in research

because they have shown an excellent device performance and have higher molar extinction coefficients with respect to N3, N179 and Black dye [10]. The enhanced absorption properties of those molecules is expected to be come from more extended conjugated system with respect to the former molecules, as shown in Fig. 2.2. [11].

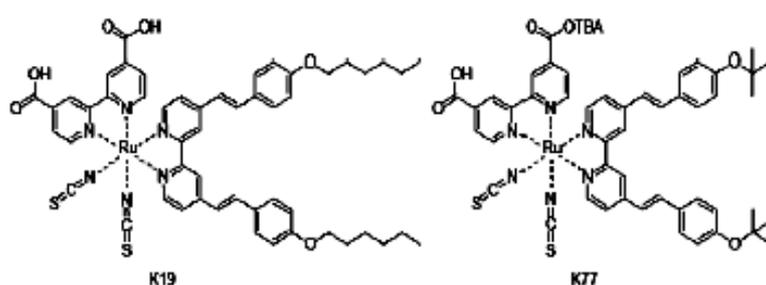


Figure 2.2 The new compound of Ruthenium based sensitizers.

However, because of the extinction coefficient lying in the range of $10^4 \text{ M}^{-1}\text{cm}^{-1}$ thick TiO_2 layers for light harvesting are required, which is not advantageous since the series resistance in the corresponding device becomes more dominant. Thus, the use of metal free dyes with high molar extinction coefficients could probably overcome this problem, especially for solid-state dye sensitized solar cells in which a thin layer of TiO_2 is required.

(b) Organic Chromophores

The interest in metal-free organic sensitizers has grown in the last few years. In 2000 Sayama et al. published a merocyanine dye (Mb(18)-N) (Fig.

2.3), which gave an efficiency of 4.2% [12]. Before this milestone, the organic dyes for DSCs performed relatively low efficiencies ($\eta < 1.3\%$) [13-16].

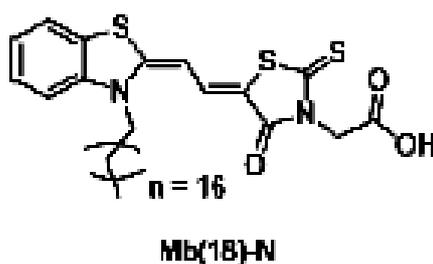


Figure 2.3 Merocyanine dye Mb(18)-N.

Organic dyes have some advantages over conventional ruthenium based chromophores as photosensitizers. For instance, they exhibit high molar extinction coefficients and are easily modified due to relatively short synthetic routes and especially low cost starting materials. The high extinction coefficients of the organic dyes are suitable for thin TiO₂ films required in solid-state devices where mass transport and insufficiently pore filling limit the photovoltaic performance [17]. This finding opens new roads for exploring new dye types.

In recent years, a great deal of research aimed at finding highly efficient and stable organic sensitizers has been carried out. A number of coumarin [18-20], indoline [21, 22], and triphenylamine [23-26] based organic

sensitizers (Fig. 2.4) have been intensively investigated and some of them have reached efficiencies in the range of 3-8% [1,16-22,24-27]. All these sensitizers are efficient and represent one strategy in developing new chromophores, namely, reaching as high efficiency as possible and dealing with possible stability issues of the chromophore at a later stage.

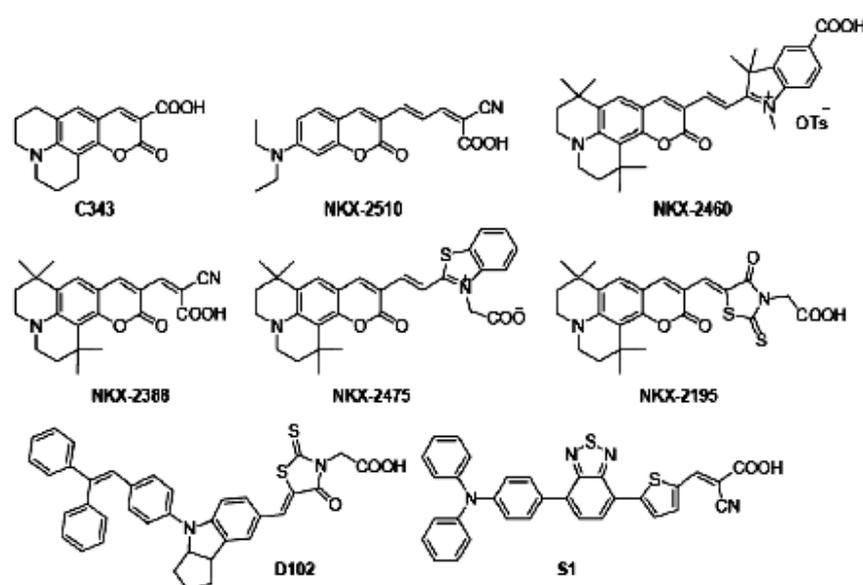


Figure 2.4 Examples of organic dyes.

2.2 Importance of Phthalocyanine dye sensitizers

Phthalocyanines (Pc's) are a prototypical class of organic porphyrin derivatives, which can combine with almost any metal in the periodic table forming highly (thermally and chemically) stable complexes, widely used,

for example, as pigments, dyes or photoelectronic devices [28,29]. These complexes have a planar structure where the central metal atom is constrained by the p-conjugated macrocyclic ligand, and the interaction between the central metal ion and the organic macrocycle determines the spin configuration of the complex.

Metal-phthalocyanines (MPc's) were already studied in the 60's and the 70's [30-34]. During the last decade, they have been object of a renewed interest due to their potential use in nanoscale technologies, such as field effect transistors, light-emitting diodes, photovoltaic and solar cells, or gas sensors [35,36]. Furthermore, MPc's deposited on metal substrates are considered prototypical models of semiconductor/metal interfaces for molecular electronic applications such as organic electronic devices [37, 38]. As prototypical single-molecule magnets, MPc's also having a wide applicability in molecular spintronics [39-41].

The electronic properties of organic molecular solids are characterized by narrow electronic bands originating from the weak, noncovalent intramolecular bonds that hold the materials together. The narrowness of the bands results in an inter band separation that is typically much larger than the bandwidth, so that the character of each band is closely related to that of the molecular orbital from which the band originates. As the band structure plays an important role in determining the electronic properties of a material, the nature of the underlying molecular orbitals can be expected

to produce observable effects in the electrical conductivity of the materials. However, it is unclear whether other phenomena (e.g., electron-electron and electron-phonon interactions or structural effects) that also play an important role in determining the electronic properties of materials can mask the effects originating from the details of the molecular orbitals.

Here, we address this issue through a comparative study of the doping dependence of the electrical conductivity of six different metal-phthalocyanine (MPc) compounds (ZnPc, CuPc, NiPc, CoPc, FePc, and MnPc), in which the electron density is controlled by means of potassium intercalation. We find that for all MPc's in which the added electrons transferred from the potassium atoms are expected to occupy orbitals centered on the ligands (ZnPc, CuPc, and NiPc), the doping dependence of the conductivity has an essentially identical shape. This shape is different from that observed in MPc materials in which electrons are also added to orbitals centered on the metal atom (CoPc, FePc, and MnPc). We conclude that in MPc compounds the characteristics of the molecular orbitals of individual molecules are directly visible in the electrical conductivity of the materials.

MPc's form a large class of organic molecules [42] that is ideally suited to investigate the relation between electrical conductivity and molecular orbitals. They consist of a metal atom located at the center of a planar ligand shell formed by carbon, nitrogen, and hydrogen atoms, with the

metal atom determining the energy and the degeneracy of the molecular orbitals [43-45]. The different individual MPc molecules are nearly isostructural, and also, their crystal structure only exhibits minor differences; this makes structural effects an unlikely origin of differences in the conductivity of different MPc compounds. Finally, MPc's have been the subject of thorough investigations in the past [45,46], and much is known about their electronic properties, which facilitate the rationalization of the experimental observations.

Doping MPc materials with electrons rather than with holes is crucial for our investigations for two main reasons. First, in holedoped MPc compounds, past systematic investigations have shown that the holes always reside on the same molecular orbital centered on the ligands. This prevents the possibility of varying the molecular orbital occupied by the charge carriers responsible for electrical conductivity. On the contrary, in electron-doped MPc's, the electron can occupy either a ligand or a metal orbital, depending on the specific molecule considered [43]. Second, it is known that it is possible to transfer a larger amount of charge by reducing [48,49] rather than by oxidizing MPc's, so that electron doping gives experimental access to a much larger interval of charge density as compared to hole doping [46,47]. So far, however, electron-doped molecular compounds have remained vastly unexplored, probably because their sensitivity to oxidizing agents increases the technical difficulties involved in their investigation.

2.3 Methods to optimize the metal free organic dyes

There are various methods to compute the electronic structure and to study theoretically the molecular properties of dyes. Some methods which can be adopted to optimize the selected dyes for using them in DSSC are discussed in this part.

2.3.1 Electronic structure theory

At the heart of quantum chemistry is the famous Schrödinger equation,

$$\hat{H}_{tot}\Psi_{tot} = E_{tot}\Psi_{tot} \quad (2.1)$$

Here expressed in a time-independent non-relativistic form. Ψ_{tot} is the total wave function which depends on the electronic and nuclear coordinates, E_{tot} is the total energy, and \hat{H}_{tot} is the Hamiltonian of the system, containing the kinetic and potential energy operators for all particles. In most quantum chemical calculations the Born-Oppenheimer approximation is invoked, which separates the motions of nuclei and electrons, so that an electronic Schrödinger equation for fixed nuclei is obtained,

$$\hat{H}_{elec}\psi_{elec} = E_{elec}\psi_{elec} \quad (2.2)$$

which only depends parametrically on the nuclear positions. Historically, most quantum chemical calculations have been based on the HF approximation to solve the electronic Schrödinger equation. In HF theory, each electron is described by a spin-specific one-electron function, a spin orbital constructed as a product of a spatial orbital and a spin function, and Ψ_{elec} is expressed in the form of a single Slater determinant of spin orbitals. A set of one-electron equations known as the HF equations is obtained by minimizing the energy of the HF trial wave function based on the variational principle, which states that a trial wave function has an energy that is higher than or equal to the exact energy. These equations have to be solved iteratively until self-consistency using the self-consistent field (SCF) procedure, because the operators in these equations depend on the orbitals that one is seeking.

In practical calculations, the HF orbitals can be defined as restricted, where electrons of different spin are, pair wise, described by a common spatial orbital, or as unrestricted where each electron has its own spatial distribution. The HF method generates solutions to the electronic Schrödinger equation, where the real electron-electron interaction is replaced by an average interaction. The consequence of this replacement is that the correlation of electrons' motion is not described properly. The correlation of electrons having the same spin is partially accounted for via an exchange interaction, but the correlation of electrons having opposite spins is not described. The exchange interaction is a non-classical

interaction between two electrons with the same spin. A good description of electron correlation is important when calculating molecular properties. Hence, it is usually required to improve the HF description in order to obtain results that compare quantitatively, or even qualitatively, with experimental results.

2.3.2 Density Functional Theory

The Density Functional Theory (DFT) was introduced by Hohenberg-Kohn in 1964. The DFT is presently the most successful (and also the most promising) approach to compute the electronic structure of matter. Its applicability ranges from atoms, molecules and solids to nuclei and quantum and classical fluids. In its original formulation, the density functional theory provides the ground state properties of a system, and the electron density plays a key role. DFT predicts a great variety of molecular properties: molecular structures, vibrational frequencies, atomization energies, ionization energies, electric and magnetic properties, reaction paths, etc.

The original density functional theory has been generalized to deal with many different situations: spin polarized systems, multi component systems such as nuclei and electron hole droplets, free energy at finite temperatures, superconductors with electronic pairing mechanisms,

relativistic electrons, time-dependent phenomena and excited states, bosons, molecular dynamics, etc.

2.3.3 The Hartree-Fock approximation

Suppose that ψ_0 (the ground state wave function) is approximated as an antisymmetrized product of N orthonormal spin orbitals, $\psi_i(x)$, each a product of a spatial orbital $\phi_k(\mathbf{r})$ and a spin function $\sigma(s) = \alpha(s)$ or $\beta(s)$, the Slater determinant

$$\psi_0 \approx \psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1^G(x_1) & \psi_2^G(x_1) & \dots & \psi_N^G(x_1) \\ \psi_1^G(x_2) & \psi_2^G(x_2) & \dots & \psi_N^G(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1^G(x_N) & \psi_2^G(x_N) & \dots & \psi_N^G(x_N) \end{vmatrix} \quad (2.3)$$

The Hartree-Fock approximation is the method whereby the orthogonal orbitals ψ_i are found that minimize the energy for this determinantal form of ψ_0 :

$$E_{HF} = \min_{(\psi_{HF} \rightarrow N)} E[\psi_{HF}] \quad (2.4)$$

The expectation value of the Hamiltonian operator with HF is given by

$$E_{HF} = \langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle = \sum_{i=1}^N H_i + \frac{1}{2} \sum_{ij=1}^N (J_{ij} - K_{ij})$$

$$H_i \equiv \int \psi_i^*(x) \left[-\frac{\hbar^2}{2m} \nabla^2 - V(x) \right] \psi_i(x) dx \quad (2.5a, b)$$

defines the contribution due to the kinetic energy and the electron-nucleus attraction and

$$J_{ij} = \iint \psi_i^*(x_1) \psi_j(x_1) \frac{1}{r_{12}} \psi_j^*(x_2) \psi_i(x_2) dx_1 dx_2$$

$$K_{ij} = \iint \psi_i^*(x_1) \psi_j(x_1) \frac{1}{r_{12}} \psi_i(x_2) \psi_j^*(x_2) dx_1 dx_2 \quad (2.6a, b)$$

The integrals are all real, and $J_{ij} \geq K_{ij} \geq 0$. The J_{ij} are called Coulomb integrals, the K_{ij} are called exchange integrals. We have the property $J_{ii} = K_{ii}$. The variational freedom in the expression of the energy is in the choice of the orbitals. The minimization of the energy functional with the normalization conditions $\int \psi_i^*(x) \psi_j(x) dx = \delta_{ij}$ leads to the Hartree-Fock differential equations

$$\hat{f} \psi_i = \epsilon_i \psi_i, \quad i = 1, 2, \dots, N \quad (2.7)$$

These N equations have the appearance of eigenvalue equations, where the Lagrangian multipliers ϵ_i are the eigenvalues of the operator \hat{f} . The Fock operator \hat{f} is an effective one-electron operator defined as

$$\hat{f} = -\frac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}} + V_{HF}(i) \quad (2.8)$$

The first two terms are the kinetic energy and the potential energy due to the electron-nucleus attraction. $V_{HF}(i)$ is the Hartree-Fock potential, the average repulsive potential experienced by the i^{th} electron due to the remaining $N-1$ electrons, and it is given by

$$V_{HF}(x_1) = \sum_i^N \left(\hat{J}_j(x_1) \right) - K_j(x_1)$$

$$\hat{J}_j(x_1) = \int \frac{|\psi_j(x_2)|^2}{r_{12}} dx_2$$

$$K_j(x_1) = \int \frac{\psi_j^*(x_2)\psi_j(x_2)}{r_{12}} dx_2 \quad (2.9a, b)$$

The Coulomb operator \hat{J}_j represents the potential that an electron at position \vec{r}_1 experiences due to the average charge distribution of another electron in spin orbital ψ_j . The second term in equation is the exchange contribution to the HF potential. It has no classical analog and it is defined through its effect when operating on a spin orbital:

$$K_j(x_1)\psi_j(x_1) = \int \psi_j^*(x_2)\psi_j(x_2) \frac{1}{r_{12}} dx_2 \psi_j(x_1) \quad (2.10)$$

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The HF potential is non-local and it depends on the spin orbitals. Thus, the HF equations must be solved self-consistently. The Koopman's theorem (1934) provides a physical interpretation of the orbital energies: it states that the orbital energy ϵ_i is an approximation of minus the ionization energy associated with the removal of an electron from the orbital ψ_i , i.e. $\epsilon_i \approx E_N - E_{N-1} = -IE(i)$. The electron density is the central quantity in DFT. It is defined as the integral over the spin coordinates of all electrons and over all but one of the spatial variables ($\mathbf{x} = \mathbf{r}, s$)

$$\rho(\mathbf{r}) = N \int \dots \int |\Psi(x_1^G, x_2^G, \dots, x_N^G)|^2 ds_1 dx_2 \dots dx_N \quad (2.11)$$

$\rho(\mathbf{r})$ determines the probability of finding any of the N electrons within volume element $d\mathbf{r}$.

Some properties of the electron density: $\rho(\mathbf{r})$ is a non-negative function of only the three spatial variables which vanishes at infinity and integrates to the total number of electrons:

$$\rho(\mathbf{r} \rightarrow \infty) = 0 \quad \int \rho(\mathbf{r}) d\mathbf{r} = N$$

$\rho(\mathbf{r})$ is an observable and can be measured experimentally, e.g. by X-ray diffraction.

At any position of an atom, the gradient of $\rho(\vec{r})$ has a discontinuity and a cusp results:

$$\lim_{r_A \rightarrow 0} [\nabla_r + 2Z_A] \bar{\rho}(r) = 0 \quad (2.12)$$

where Z is the nuclear charge and $\bar{\rho}(\vec{r})$ is the spherical average of $\rho(\vec{r})$.

The asymptotic exponential decay for large distances from all nuclei:

$$\bar{\rho}(r) \approx \exp[-2\sqrt{2I}|r|] \quad (2.13)$$

where I is the exact ionization energy

(i) The Thomas-Fermi model

The conventional approaches use the wave function ψ as the central quantity since it contains the full information of a system. However, ψ is a very complicated quantity that cannot be probed experimentally and that depends on $4N$ variables, N being the number of electrons.

The Thomas-Fermi model: the first density functional theory (1927). Based on the uniform electron gas, they proposed the following functional for the kinetic energy:

$$T_{TF}[\bar{\rho}(r)] = \frac{3}{10} (3\pi^2)^{2/3} \int \bar{\rho}^{5/3}(r) dr \quad (2.14)$$

The energy of an atom is finally obtained using the classical expression for the nuclear-nuclear potential and the electron-electron potential:

$$E_{TF}[\rho^G] = \frac{3}{10} (3\pi^2)^{2/3} \int \rho^G(\mathbf{r}) d\mathbf{r} - Z \int \frac{\rho^G(\mathbf{r})}{r} d\mathbf{r} + \frac{1}{2} \iint \frac{\rho^G(\mathbf{r}_1)\rho^G(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \quad (2.15)$$

The energy is given completely in terms of the electron density. In order to determine the correct density to be included in Eq. (2.15), they employed a variational principle. They assumed that the ground state of the system is connected to the $\rho(\vec{r})$ for which the energy is minimized under the constraint of $\int \rho(\vec{r}) d\vec{r} = N$.

The main drawback with the HF based electronic structure methods that include electron correlation is that they become too time-consuming for most realistic molecular systems. This fact is the main motivation for using density functional theory (DFT) which has the inherent capability of treating electron correlation at a much lower computational cost. In DFT the basic variable, the wave-function Ψ_{elec} , is replaced by the electron density $\rho(\mathbf{r})$, which is a function of only 3 spatial coordinates. The energy as well as other observables of the molecular system is obtained from $\rho(\mathbf{r})$ by so-called functionals. As a consequence of the two theorems of Hohenberg and Kohn, the electron density may be considered the fundamental variable of multi-electron theory. In principle, knowing the electron density of the

ground state, the ground state energy and all ground state molecular properties are possible to calculate. The second Hohenberg-Kohn theorem shows that the energy of the electron density obeys the variational principle in the sense that among all possible candidates of electron densities, the exact density is the one that also delivers the lowest energy.

2.3.4 Basis sets

The individual orbitals Ψ_i molecular or atomic depending on the investigated system, are expanded in terms of a set of basis functions $\{\Psi_v\}$, centered on the nucleus or nuclei, $\psi_i = \sum_v c_{iv} \phi_v$ where the orbital expansion coefficients, C_{iv} are optimized during the calculation. The set of basis functions available for an expansion is called the basis set. These basis functions can be Slater type orbital (STO) functions which are similar to the orbitals obtained by the analytical solution of the Schrödinger equation for the hydrogen atom. However, a more efficient computation of two-electron integrals is achieved with Gaussian type orbital (GTO) functions.

It is therefore more common to use so-called contracted Gaussian functions, in which several primitive GTO functions are combined in a fixed, predefined linear combination. The choice of basis set is very important for the quality of the computational results. A sufficiently flexible and well-balanced basis set must be used to obtain accurate results, but accuracy and computational cost has to be weighed against each other.

2.3.5 Absorption spectra using time-dependent density functional theory

Time-dependent density functional theory (TD-DFT) is an extension of DFT to time dependent problems, such as a molecular system's interaction with a time-dependent external field. In the case of a spectroscopic measurement of an optical absorption spectrum the external field is an electromagnetic wave. Under these conditions, the effect on the system by the external field is sufficiently small to allow that the system's response is described by time dependent perturbation theory. Within this approach, the excitations are expressed in terms of ground state properties and excited states are not evaluated explicitly.

The simplest form of the interaction of the system and the electromagnetic wave is the electric dipolar interaction, giving the time dependent perturbation needed to be considered, for example, the following form:

$$H^{(1)}(t) = -\underset{G}{\mu} \cdot \underset{G}{E}(t) \quad (2.16)$$

where $\underset{G}{\mu}$ is the dipole moment operator of the electrons, and the electric field $\underset{G}{E}$ is oscillating with frequency ω in the simple case of monochromatic light. The linear response of the system to such a perturbation is described by the dynamic polarizability $\bar{\alpha}(\omega)$. Since the molecules are randomly oriented in for example solution and gas phase, the interesting quantity for

comparisons with experiments is the mean dynamic polarizability $\bar{\alpha}(\omega)$ a property that has the following form:

$$\bar{\alpha}(\omega) = \sum_I^{\text{excited states}} \frac{f_I}{\omega_I^2 - \omega^2} \quad (2.17)$$

where $\omega_I = E_I - E_0$ are the excitation energies and f_I are the oscillator strengths, which contain the transition dipole moments

$$f_I = \frac{2}{3} (E_I - E_0) \left| \langle \Psi_0 | \hat{\mu}^G | \Psi_I \rangle \right|^2 \quad (2.18)$$

The dynamic polarizability has poles (diverges) at frequencies corresponding to excitation energies. Hence, the absorption spectrum of a system can in principle be obtained as the poles and residues (numerator at the poles) of the mean dynamic polarizability [50].

It appears to be generally accepted that TD-DFT provides fairly accurate excitation energies as long as low-energy transitions involving valence states are investigated [51]. Hybrid functionals, such as B3LYP, seem to yield slightly more accurate results than simple GGA functionals especially for charge transfer states [52].

2.3.6 Polarizable continuum solvent model

In a polarizable continuum model (PCM), the molecule is surrounded by a dielectric medium, the polarizable continuum, with a given dielectric constant ϵ . This medium is polarized in response to the charge distribution (nuclei and electrons) that it experiences and produces an electric field, called a reaction field, which in turn polarizes the molecule. The resulting slightly changed charge distribution alters the reaction field somewhat, which again leads to further polarization of the molecule. This process continues until equilibrium is reached.

In the PCM implemented in the Gaussian program, the reaction field is represented through charges located on the surface of the molecular cavity [53]. The molecular cavity can be created in several ways, but is generally based on interlocking Van der Waals-spheres centered at atomic positions. The surface of this cavity is smoothed (for numerical reasons) and in the PCM model approximated by many small planar surface elements (tesserae) of given area. Charges are then placed on each of the surface elements to represent the reaction field of the dielectric medium. The extent to which the medium can be polarized, and hence the ultimate strength of the reaction field is controlled by the magnitude of the dielectric constant. In this work, CPCM model of acetonitrile ($\epsilon \approx 37$) is used.

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