

Chapter 2

Density Functional Theory in the Design of Organometallics for Energy Conversion

Gemma R. Freeman and J.A. Gareth Williams

Abstract Theoretical methods based on density functional theory (DFT) and time-dependent density functional theory (TD-DFT) are increasingly used to rationalise the excited-state properties of metal complexes and to help guide the design of new materials. This chapter provides a brief introduction of the background to such methods, highlighting some of the features that need to be considered, such as the ability of functionals to deal with charge-transfer states and the challenges associated with triplet-state calculations. Examples are drawn from recent studies on (1) the ground-state and light absorption properties of ruthenium(II) complexes as sensitisers for dye-sensitised solar cells (DSSCs) and (2) the triplet excited states of luminescent platinum(II) complexes that are potential phosphors for organic light-emitting diodes (OLEDs).

Keywords Time-dependent density functional theory (TD-DFT) • Metal complexes • Phosphorescence • Iridium • Platinum • Ruthenium • Organic light-emitting diode • OLED • Dye-sensitised solar cell (DSSC)

2.1 Introduction

Metal complexes and organometallics play a key role in many devices for energy conversion, particularly those where light is involved. For example, in the new generation of display screen equipment and energy-efficient lighting – organic light-emitting diodes (OLEDs) – the use of complexes of heavy transition metals as phosphorescent emitters allows large gains in efficiency through the harvesting of otherwise wasted triplet states [1]. Meanwhile, in the reverse process of light-to-electrical energy conversion, metal complexes that absorb light to generate charge-transfer states are at the forefront of research into dye-sensitised solar cells (DSSCs) [2]. Metal complexes with long excited-state lifetimes and that are strong excited-state oxidants or reductants also attract attention in the field of ‘artificial photosynthesis’ (AP) – the conversion of light-to-chemical energy, for example, in

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photocatalysed ‘water splitting’ to generate H_2 for subsequent use as a non-polluting fuel [3].

All of these applications require certain properties of the metal complexes to be optimised. For example, in DSSCs and AP, the compounds need to absorb light very strongly, preferably across the whole of the visible region of the spectrum and into the near infrared (NIR). Moreover, they need to form the appropriate kind of excited state (e.g. metal-to-ligand charge transfer, MLCT, in the case of DSSCs) and with the correct directionality (i.e. charge transfer to one particular ligand, normally the one bound to the semiconductor). Complexes for both applications must also satisfy quite stringent requirements in terms of ground- and excited-state redox potentials, since electron transfer is a key step. Similarly, in the field of OLEDs, metal complexes are required that display phosphorescent emission from triplet states with very high efficiency (i.e. high luminescence quantum yield) and with well-defined and tunable emission maxima for use in red-green-blue (RGB) displays [4].

These requirements have led to a large number of labour-intensive synthetic projects around the world, whereby potential molecular materials are prepared in the laboratory and their photophysical and electrochemical properties then studied. Such projects have led to extensive empirical data. But theoretical methods are increasingly important in allowing such data to be interpreted, making it more useful in the informed *design* of new materials. The goal of such theoretical methods should be to allow the properties of a possible molecule to be predicted accurately and rapidly, so that synthetic effort can be directed specifically to those systems likely to show the best results.

Whilst empirical molecular mechanics [5] and semiempirical methods [6] have found utility in calculations on transition-metal complexes, the requirement for suitable parametrisation has limited their use. More common are *ab initio* techniques, in particular Hartree-Fock (HF) methods, which can provide reasonable results for second and third row transition metals [7]. These, however, become increasingly impracticable with increasing number of atoms, and density functional theory (DFT) calculations are favoured for their similar accuracy at a reduced computational cost as well as their inclusion of electronic correlation effects [8].

DFT is based on the Hohenberg-Kohn theorem, namely, that all ground-state properties – including the ground-state energy – are uniquely determined by the electron density $\rho(r)$, where r represents spatial coordinates [9]. The density and hence energy are optimised using variational procedures to determine the ground-state geometry and properties. DFT can be used to calculate both closed- and open-shell systems, although the molecules typically of interest in the field of this chapter are closed shell, and we shall limit the ensuing discussion to these cases.

The electron density $\rho(r)$ is obtained by summing over all occupied Kohn-Sham (KS) orbitals $\phi_i(r)$:

$$\rho(r) = \sum_i n_i |\phi_i(r)|^2 \quad (2.1)$$

where n_i is the orbital occupancy. The KS orbitals can then be expressed in terms of a linear combination of atomic orbitals χ_j or basis set, as in the wave function-based techniques:

$$\phi_i = \sum_j c_{ij} \chi_j \quad (2.2)$$

The orbitals $\phi_i(r)$ and their energies are obtained by solving the KS equations, which incorporate terms for the kinetic and electrostatic potential energy, as well as a term V_{XC} that describes electron exchange and correlation. Since an exact mathematical expression for V_{XC} is unknown, approximate functionals have to be used. Indeed, the availability of increasingly complex but accurate exchange-correlation functionals has been a key reason behind the rapid development and wide uptake of DFT methods over recent years. Excited states are dealt with using time-dependent DFT (TD-DFT), wherein the molecule is considered to be subject to a time-dependent perturbation arising from an oscillating electrical field associated with incident radiation. The electron density $\rho(r, t)$ becomes time dependent.

Accuracy has now reached the stage where DFT calculations may be used almost routinely in combination with experimental studies of transition-metal complexes. For example, in the field of organic light-emitting diodes (OLEDs), the widely used emissive material aluminium tris(8-hydroxyquinoline) (Alq_3), used in the landmark report of Tang and VanSlyke [10], was studied by a number of groups around the turn of the century, with reasonable correlation with experiment [11–13]. Similarly, cyclometallated iridium(III) complexes – phosphorescent emitters in contemporary commercial OLED display screens used in some mobile phones, for example – have been extensively investigated using TD-DFT methods [14]. The same methods have also been applied to related complexes with other metal ions such as platinum(II) and gold(III) [15, 16]. There is also an increasing interest in modelling DSSC dyes using theoretical methods, not just the light absorption properties of the isolated molecules but also as semiconductor-adsorbed species and their redox potentials [17].

In this chapter, following a brief overview of the principles, a selection of examples will be presented of the application of DFT and TD-DFT methods to metal complexes for use in DSSCs and OLEDs. This is a very active area, and the aim is – of course – not to be comprehensive but rather to convey a flavour of the activity and some of the challenges. A number of cyclometallated complexes will be used as examples, reflecting not only the attractiveness and increasing importance of such compounds but also the authors’ own research interests.

2.2 DFT Methods for Metal Complexes and Organometallics

The way in which DFT is carried out on metal-containing molecules is essentially no different from its application to small organic molecules. Nevertheless, there are some commonly encountered issues, such as the choice of basis set for heavy metal ions and the importance of charge-transfer states in the field, which raise challenges. Such points will be highlighted in specific cases in subsequent sections. At this stage, it may be useful to briefly consider the approach in more general terms.

2.2.1 *Choice of Functional*

Since the ability to probe excited states is key to the applications in mind (absorption or emission of light), the chosen functionals should be able to deal well with excitation energies. Functionals that employ generalised gradient approximations (GGAs), such as PBE, systematically underestimate excitation energies and are typically inappropriate [18]. The introduction of exact exchange helps to deal with these deficiencies. The exact orbital exchange in DFT is the HF exchange energy expression, evaluated using KS orbitals. Global hybrid (GH) functionals employ a fixed amount of exact orbital exchange, α . Examples include B3LYP ($\alpha = 20\%$) [19, 20] and PBE0 ($\alpha = 25\%$), which have emerged as the most popular of the functionals [21].

Nevertheless, such GH functionals do systematically underestimate excitation energies associated with through-space charge-transfer transitions. Ironically, it is precisely such charge-transfer states that are particularly important in energy conversion applications. In DSSCs, the formation of a charge-transfer state by the sensitiser upon the absorption of light is the first step in charge separation, prior to injection of an electron into the semiconducting material such as TiO_2 [22]. Meanwhile, in phosphorescent OLEDs and LECs, it is well established that a high degree of metal-to-ligand charge-transfer (MLCT) character is typically required in the excited state, in order to promote the radiative decay of the triplet states by introducing the spin-orbit coupling effect of the metal ion [23]. Range-separated hybrid (RSH) or Coulomb-attenuated functionals are of interest in this connection [24]. They have been shown to improve calculation of long-range, charge-transfer-type excitation energies, but maintain a good approximation of localised excitations. They work by varying the amount of the exact orbital exchange as a function of the interelectron distance, r_{12} ; for example, CAM-B3LYP has an initial α of 19 %, increasing to 65 % at high r_{12} [25].

2.2.2 *Choice of Basis Sets*

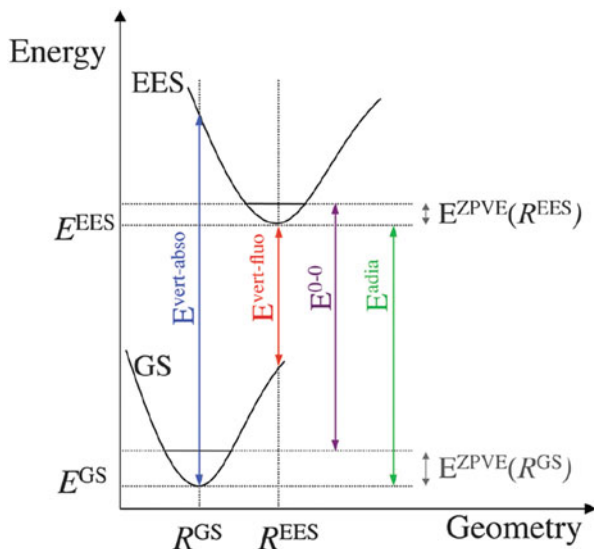
For complexes of low-atomic-weight metals, such as those of Al^{3+} and Zn^{2+} , for example, it is usual to use a standard, double- ζ quality, basis set such as 6-31G or cc-PVDZ for all atoms in the molecule, as typically used for organic molecules. In the case of complexes of heavy metals, particularly third row transition-metal ions such as Ir(III) or Pt(II), it is more common to treat the metal using a different basis set from the rest of the atoms, replacing the large number of core electrons of the metal by an ‘effective core potential’ (ECP). Since these inner electrons are not involved in bonding, very little loss of accuracy is incurred, but there is a large decrease in calculation time. The more significant outer core [e.g. $(5s)^2(5p)^6$ in the case of Ir(III)] and valence electrons [$(5d)^6$ for Ir(III)] are still included. The Los Alamos National Laboratory 2-double- ζ (LANL2DZ) basis set is popular for such metals, which incorporates an ECP. Other variants include the Stuttgart 1997 ECP.

2.2.3 *Potential Energy Surfaces and Optical Transitions*

The first step in applying DFT methods to metal complexes is normally to optimise the ground-state geometry. This process involves the evaluation of the energy of the molecule by DFT and minimisation according to structure (bond lengths, bond angles, torsions, etc.). For most molecules of interest in the field, the ground states are normally singlet states with no unpaired electrons. The large ligand-field splitting associated with second and third row transition metals ensures low-spin configurations. Where a crystal structure of the molecule of interest is available, the use of the atomic coordinates within the crystal as a starting point can help to reduce the computational time. In some cases, however, crystal packing effects and intermolecular interactions can influence molecular geometry, so some care should be exercised when using this approach, in case a local rather than global minimum is determined. Calculation of the vibrational frequencies of the optimised structure normally provides evidence if this is the case, as revealed by negative (imaginary) values, and this check is strongly recommended. Restarting the calculation from a modified geometry will typically lead to the correct structure.

Having obtained the optimised (i.e. global energy-minimised) S_0 structure, TD-DFT can then routinely be applied to determine the energies and oscillator strengths of spin-allowed ($S_0 \rightarrow S_n$) transitions and the energies of spin-forbidden transitions ($S_0 \rightarrow T_n$) at the S_0 geometry, corresponding to the process of light absorption. (Note that the successful incorporation of spin-orbit coupling into such calculations remains an elusively challenging task, such that oscillator strengths for $S_0 \rightarrow T_n$ transitions are unlikely to be very meaningful in commercial packages.) Jacquemin and co-workers have outlined the different methods that are commonly used for the calculation of $S_0 \rightarrow S_1$ excitation energies, which are illustrated in Fig. 2.1 [26, 27]. TD-DFT calculation of $E^{\text{vert-abso}}$ gives the energy

Fig. 2.1 Jablonski diagram representing a ground state (GS) and an excited electronic state (EES) and the different possible methods for calculating excitation energies (Reprinted with permission from [27]. © 2012 American Chemical Society)



of the lowest-energy absorption process: in principle, this should correspond to the longest wavelength band in the absorption spectrum. The same calculation at the S_1 excited-state geometry, $E^{vert-fluo}$, corresponds to fluorescence. This quantity is smaller than $E^{vert-abso}$ due to the relaxation of the excited state (typically on a timescale of picoseconds) prior to emission (typically a nanosecond timescale). The difference between the two minima in the scheme of Fig. 2.1 is the adiabatic energy, E^{adia} . It is occasionally used to calculate emission energies [28] but will generally lead to values that are too high, owing to the typically shallower potential energy surface (PES) of the excited state and smaller zero-point energy.

In order to model phosphorescence from the triplet state, the $S_0 \rightarrow T_1$ excitation energy at the T_1 geometry should be calculated. It is important to note that DFT applies rigorously to the lowest state of *any* spin multiplicity; thus, the geometry of the T_1 state can be obtained directly, just as for the S_0 state, and the TD-DFT calculation then performed. It is, however, more likely than for the S_0 that local minima may inadvertently be found as opposed to the true minimum, owing to the typically flatter profile of the PES. It is common practice to model triplet emission by calculating the $S_0 \rightarrow T_1$ excitation energy at the S_0 (as opposed to T_1) geometry [29, 30], since it saves on computational time, requiring only one geometry optimisation. Such values will, however, normally be too high in energy, and good correlation with experiment may be fortuitous through cancellation of errors.

Calculations of the $S_0 \rightarrow T_1$ excitation at the T_1 geometry can, however, sometimes produce excitation energies that are implausibly low in energy or even imaginary. This phenomenon has recently been discussed in small molecules and ascribed to ‘triplet instabilities’ [31, 32]. It is a well-known deficiency of HF theory [33, 34], and thus it is perhaps unsurprising that DFT functionals that incorporate some degree of exact orbital exchange will suffer from similar difficulties with

triplet states. The use of the Tamm-Dancoff approximation (TDA) is recommended for calculating excitation energies with low triplet stabilities [35, 36]. The TDA corresponds to setting $B=0$ in the generalised eigenvalue equations (2.3); i.e. allowing only excitation between occupied-virtual orbital pairs (given by the eigenvector X) as opposed to conventional TD-DFT, where virtual-occupied de-excitation contributions (Y) are also permitted. Since A is Hermitian, the occurrence of imaginary excitation energies is precluded. To date, however, the TDA has been little applied to metal complexes [37]:

$$\begin{pmatrix} A & B \\ B & A \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix}. \quad (2.3)$$

2.2.4 Modelling Solvent

DFT calculations are normally performed in the gas phase. Since such conditions are difficult to reproduce experimentally and different solvents can have a profound effect on the optical properties, it is often desirable to introduce solvent into the calculations. The two main approaches for the estimation of solvent effects are explicit and implicit models. The former treats every solvent molecule individually, calculating their interaction with one another and the compound of interest. Though occasionally applied to small molecule systems, it is computationally demanding and not used routinely for larger systems such as metal complexes [38].

Implicit solvent models, on the other hand, describe the volume around the compound of interest as a structureless continuum. For example, the polarisable continuum model (PCM) [39] is often used in calculations of large molecules, including third row transition-metal complexes [40–42]. This approach omits specific solvent interactions but describes the polarity of the environment.

2.3 Examples in Light-to-Electrical Energy Conversion: DSSCs

2.3.1 Background and Brief Guide to What Calculations Can Offer

In a conventional inorganic semiconductor solar cell or a bulk heterojunction cell, the materials are responsible for absorbing light as well as participating in charge transport. In a DSSC, the two functions of light absorption and charge transport are separated. A dye coated onto a semiconductor is used to absorb light and initiates the transfer of an electron into the semiconductor, which functions as the charge transporter. The basic design and components of a DSSC are shown in Fig. 2.2. After the absorption of light to generate the excited state, the dye injects an electron

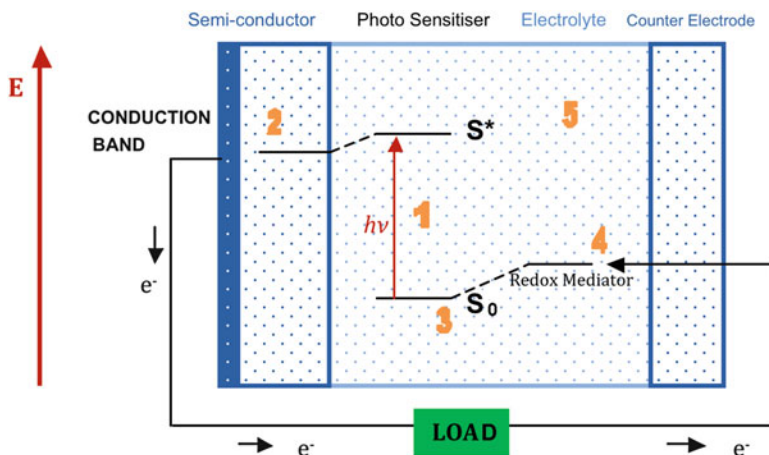
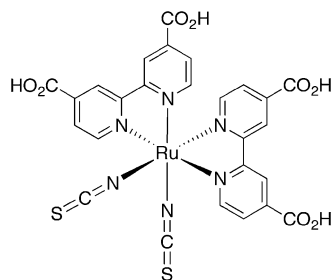


Fig. 2.2 Simplified diagram showing the mode of action of a dye-sensitised solar cell (DSSC). Key processes are (1) excitation of the sensitizer by light absorption, (2) injection of an electron into the semiconductor and hence circuit, (3) reduction of the oxidised sensitizer by the reduced form of the redox mediator and (4) reduction of the oxidised form of the mediator by incoming electrons from the counter electrode

into the semiconductor which subsequently flows around the circuit. The oxidised dye is in turn reduced by electrons from the counter electrode, through the intermedicacy of a redox electrolyte, typically I^-/I_3^- , which acts as an electron shuttle.

The most successful and widely investigated dyes are based on ruthenium-bipyridine complexes related to $[\text{Ru}(\text{bpy})_3]^{2+}$ ($\text{bpy} = 2,2'$ -bipyridine). This is because their lowest-energy excited states are archetypal MLCT states: the absorption of light has already induced an initial charge separation in a well-defined direction, with transient oxidation of the Ru(II) centre, and reduction of one of the ligands (normally that on which the LUMO is based). If the ligand to which the electron transfer occurs is attached to the semiconductor surface, then the electron can move from the ligand onto the semiconductor, before the regeneration of the ground state occurs though radiative or other non-radiative decay processes. Other reasons for the success of such complexes relate to the suitability of their energy levels (redox potentials) in the ground and excited state: the HOMO and LUMO should be higher in energy than the valence band edge and conduction band edge, respectively, of the semiconductor. The so-called N3 dye (Fig. 2.3) developed by Grätzel and co-workers has become a benchmark compound in the area. The carboxylate groups allow for binding to a TiO_2 surface, and the σ -donating thiocyanate groups help to raise the energy of the metal d-orbitals and thus lower the energy of the MLCT transition compared to $[\text{Ru}(\text{bpy})_3]^{2+}$, shifting the absorption band towards the red.

Fig. 2.3 The structure of the benchmark Ru (II) complex known as the N3 dye



Even from this very brief discussion, it is clear that TD-DFT calculations should be able to help rationalise the performance of known dyes and inform the design of new dyes by allowing:

1. The nature of the lowest-energy excited state to be deduced; e.g. is it MLCT as required, or does it have undesirable ligand-centred $\pi-\pi^*$ or metal-centred (d-d) character?
2. The location of the acceptor in the CT process (often the LUMO) to be identified; e.g. is it based on the ligand carrying the anchoring groups – through which the complex will bind to the semiconductor – as desired, or on one of the other ligands, which will lead to poorer performance?
3. The absorption spectrum to be deduced; e.g. does the spectrum extend to long wavelengths and with the high extinction coefficients required for good efficiencies (determined by oscillator strengths)?
4. An assessment of other non-radiative decay pathways open to the excited state that may compete with electron injection.
5. Frontier orbital energy levels/electrochemical potentials to be determined.
6. Interaction of the dye with the electrolyte to be assessed.

2.3.2 *Redshifting the Absorption and Localisation of the LUMO*

Liao and co-workers have recently considered the simulation of the absorption spectrum of the N3 dye, comparing results obtained using B3LYP and CAM-B3LYP, and with a range of basis sets, either with or without a solvent included [43]. They found that the inclusion of solvent (DMF) using a PCM led to better agreement with the experimental data (Fig. 2.4). The lowest-energy bands were found to have mixed MLCT/LLCT character, with excitations originating from MOs localised mainly on the Ru and NCS ligands into the π^* orbitals of the bipyridines, as expected. Notably, B3LYP appears to underestimate the energy of these bands, in line with the long-range CT assignment, whereas CAM-B3LYP deals with this issue, but leads to an overestimation of the energy. Using CAM-B3LYP with a PCM, and LANL2DZ for the Ru(II) ion, the use of basis

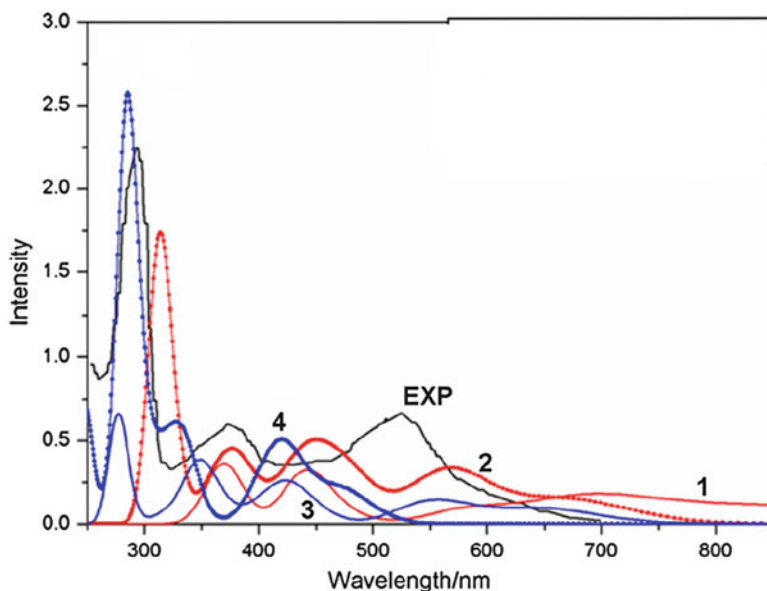


Fig. 2.4 Experimental UV-visible absorption spectra of N3 dye in DMF solvent (EXP) and simulated spectra using TD-DFT: (1) B3LYP gas phase, (2) B3LYP with PCM, (3) CAM-B3LYP gas phase and (4) CAM-B3LYP with PCM (basis set = LANL2DZ for Ru, 3-21G* for other atoms in each case) (Reprinted with permission from [43]. © 2013 Elsevier)

sets that add a set of diffuse functionals on other atoms (e.g. 6-311 + G*) was found to give improved results.

One of the limitations of dyes such as N3 is that the absorption (and hence the incident photon conversion efficiency or IPCE) falls off rapidly in the red region of the spectrum. Researchers are actively seeking to extend the absorption of such dyes into the red and NIR regions. One way to achieve this is to increase the extent of conjugation in one of the donor ligands and/or to append electron-rich substituents. For example, a number of complexes incorporating thiophene-appended bipyridine ligands have been explored. Liu et al. carried out TD-DFT calculations and an orbital analysis on a series of complexes including those of Fig. 2.5 [*op. cit.*]. Despite the redshift induced by thiophene pendants, the amount of photoinduced charge transfer (Δq) towards the bipyridine dicarboxylate (dcbpy) acceptor from the rest of the molecules in the S_1 state does not significantly increase as the conjugation length in the ancillary ligand increases from T to TT to TTT. However, a notable observation is that in some higher excited states S_n ($n > 1$), the thiophene-appended ancillary ligand (AL) actually acts as an acceptor: increased conjugation lowers the vacant orbitals on these units. Such an effect will clearly be detrimental to the charge injection efficiency, as the electron should be transferred to the dcbpy. Interestingly, the change of one of the two carboxylates to a CN unit ensures that the bpy remains the acceptor, as shown in Fig. 2.6.

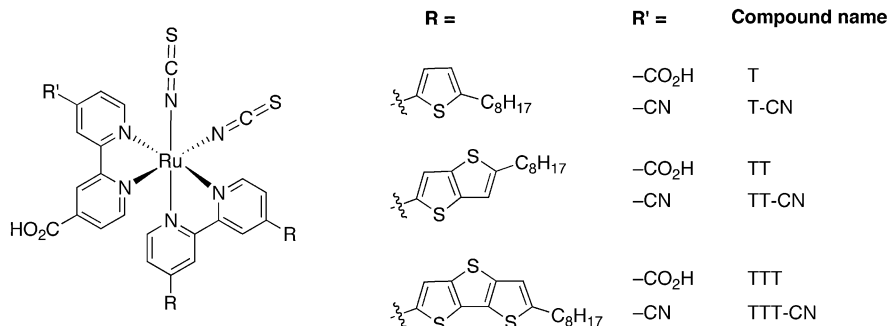


Fig. 2.5 Structures of thiophene-appended variants of the N3 dye investigated by Liu et al. [43]

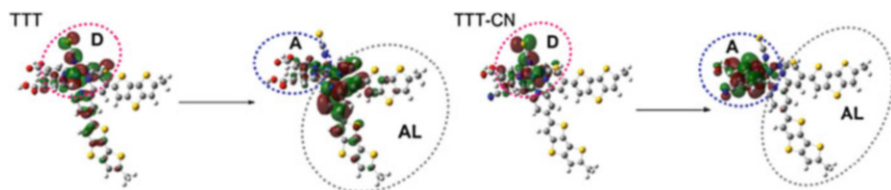


Fig. 2.6 Natural transition orbitals for the $S_0 \rightarrow S_3$ transition of TTT (left) and TTT-CN (right), determined by TD-DFT using CAM-B3LYP. The circled groups D and A are the donor (metal/thiocyanate) and acceptor (dcbpy), respectively, whilst AL indicates the thiophene-appended 'ancillary' ligands (Reprinted with permission from [43]. © 2013 Elsevier)

Another interesting example comes from the recent work by Gros and colleagues, who have been exploring the utility of dithienylpyrrole (DTP) pendants for redshifting the absorption of N3-like dyes [44, 45]. Complexes such as those shown in Fig. 2.7 have been prepared. They show significantly enhanced extinction coefficients compared to N3 and good coverage over the visible spectrum. The tris-heteroleptic complex **C4** with the thienyl-linked DTP, in particular, displays significant absorption to long wavelengths > 700 nm. Nevertheless, these complexes were found to display only low IPCE values, using either TiO₂ or SnO₂ as the semiconductor, indicating that charge injection is inefficient. The possible explanation is that this might be due to the localisation of the electron in the MLCT state in the 'wrong' ligand – i.e. the DTP-appended bipyridine as opposed to the dcbpy ligand was subsequently confirmed by TD-DFT study, supported by transient absorption spectroscopy. The virtual natural transition orbitals of **C1**, for example (Fig. 2.8), show the confinement of the excited electron on the metal- and DTP¹-appended ligand, with no participation of the dcbpy ligand. In the case of **C4**, although the lowest-energy transition does show the desired localisation of the excited electron on the dcbpy ligand, other higher-energy transitions with much higher oscillator strengths again suffer from the problem of localisation of the electron on the DTP² ligand, remote from the semiconductor surface.

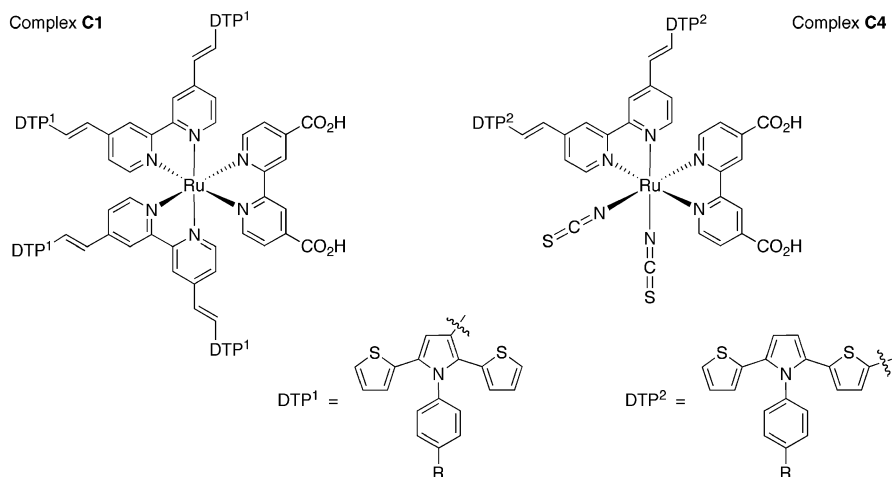


Fig. 2.7 Ru(II) complexes **C1** and **C4** incorporating dithienylpyrrole units studied by Gros and co-workers [45]

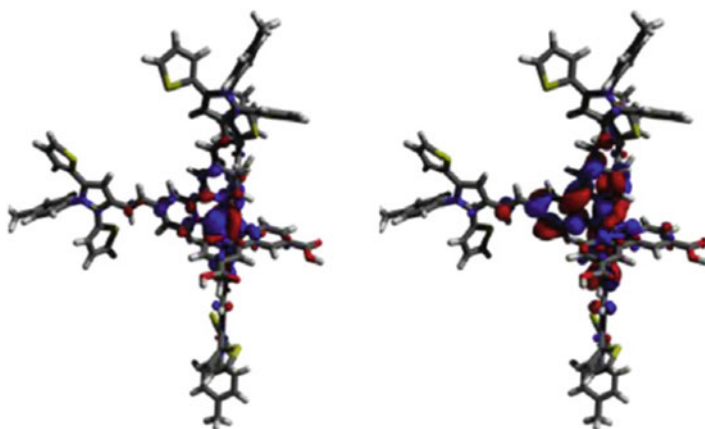


Fig. 2.8 Natural transition orbitals for complex **C1** at 488 nm, occupied (*left*) and virtual (*right*) orbitals. A similar picture is obtained at 512 nm (Reprinted with permission from [45]. © 2014 Elsevier)

2.3.3 Cyclometallation Versus Monodentate Thiocyanate Ligands

Many of the most thoroughly investigated ruthenium-based DSSC dyes contain monodentate thiocyanate ligands. As noted above, the thiocyanates raise the energy of filled metal orbitals compared to $[\text{Ru}(\text{bpy})_3]^{2+}$ and also lower the symmetry, leading to a broader absorption band. Nevertheless, the NCS ligands have

drawbacks: they make it difficult to further tune the HOMO, and they can compromise the long-term chemical stability of the complex, one of the biggest issues limiting widespread uptake of the technology.

The past few years has witnessed increasing interest in cyclometallated ligands in place of the thiocyanates. The archetypal cyclometallating ligand in the field is 2-phenylpyridine (ppyH), which binds as an anionic $N^{\wedge}C$ ligand, forming a 5-membered chelate ring, isoelectronic with neutral bpy. The resemblance between the electronics/MO energy levels of such complexes and their thiocyanate analogues has been highlighted by Berlinguette and co-workers, using a combination of experimental and DFT data [46]. It can be seen (Fig. 2.9) that the introduction of the ppy ligand in place of a bpy in $[\text{Ru}(\text{bpy})_3]^{2+}$ has a similar effect to thiocyanate ligand, actually destabilising the filled metal orbitals to a slightly greater extent and leading to a pronounced long-wavelength tail in the absorption spectrum (Fig. 2.10) [47]. A similar analysis has been carried out by Grätzel and co-workers [48]. Notably, modification of the phenyl ring of the cyclometallating ligand (e.g. introduction

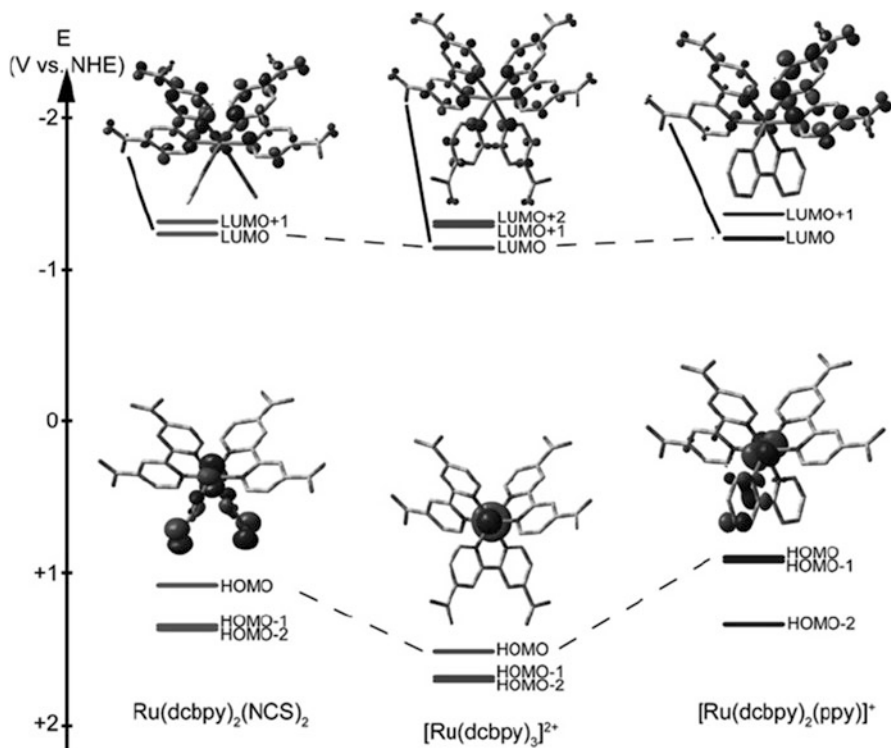
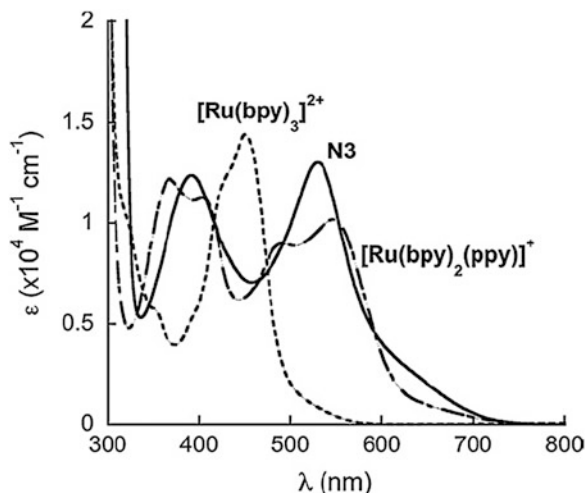


Fig. 2.9 Energy level diagram and selected MOs for the N3 dye (left), $[\text{Ru}(\text{dcbpy})_3]^{2+}$ (centre) and the cyclometallated complex $[\text{Ru}(\text{dcbpy})_2(\text{ppy})]^+$. The positions of HOMO and LUMO energy levels are from experimental measurements; other energy levels calculated by TD-DFT and adjusted relative to the HOMO and LUMO (Reprinted with permission from [46]. © 2012 Elsevier)

Fig. 2.10 Experimental UV-visible absorption spectra of the three complexes of Fig. 2.9 in MeCN at 298 K (Reprinted with permission from [46]. © 2012 Elsevier)



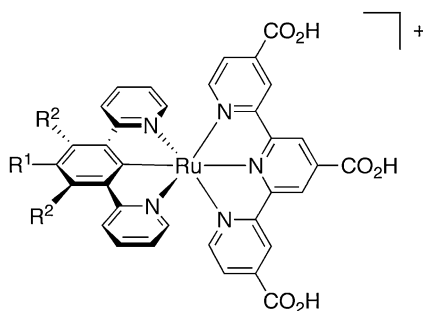
of different substituents) can be used to provide subtle control over the energy of the HOMO [49]. Chen et al. have used a similar strategy with a ‘pseudo-cyclometallate’ – an anionic $N^{\wedge}N^{-}$ -binding pyrazolylpyridine ligand [50].

There has been considerable interest in applying DFT methods to dyes bound to the semiconductor surface, as opposed to studies on the isolated dye molecules in vacuo. The methods employed for this purpose can be divided mainly into two types. In one type, periodic DFT calculations with plane-wave methods are carried out, where the TiO_2 101 surface is created by cleaving the TiO_2 anatase crystal [51]. The other method treats the semiconductor as a ‘molecular’ species – a nanoparticle $(TiO_2)_n$, with n typically in the range 16–82 (e.g. [52]). Although the smaller nanoparticles do not necessarily allow all binding modes of the dye to be identified, they offer computational advantages. Calculations on dye- $(TiO_2)_n$, including TD-DFT calculations, are then carried out as isolated molecules in the gas phase or in solvent.

Singh and co-workers have very recently applied such methods to a series of cyclometallated Ru(II) complexes incorporating tridentate ligands (Fig. 2.11) [53]. Complex **M3** showed the best DSSC performance with an experimental overall energy conversion efficiency, η , of 7.1 %. TD-DFT calculations on the isolated complex showed that the presence of the cyclometallating ligand on one side of the molecule leads to high directionality in the charge-transfer process; for example, the most intense singlet transition in the low-energy region is mainly HOMO–1 $\rightarrow$ LUMO + 1 in character: the former spans the metal (56 % contribution) and the two ligands, whilst the latter is almost exclusively on the terpyridine ligand (Fig. 2.12). It is thanks to the electron-donating substituents on the cyclometallated ligand, which raise HOMO–1, that **M3** has the most redshifted absorption bands and the highest η amongst the four complexes.

The complex was modelled on $(TiO_2)_{38}$ using plane-wave methods [*op. cit.*]. The bidentate bridging mode of binding via two carboxylates (Fig. 2.13b) was found to be energetically more favoured than that through only one carboxylate group (Fig.

Fig. 2.11 Structures of the cyclometallated, bis-terdentate Ru(II) complexes studied by Singh and co-workers [53]



$R^1 = R^2 = H$ **M1**

$R^1 = H, R^2 = CH_3$ **M3**

$R^1 = CH_3, R^2 = H$ **M2**

$R^1 = CO_2H, R^2 = H$ **M4**

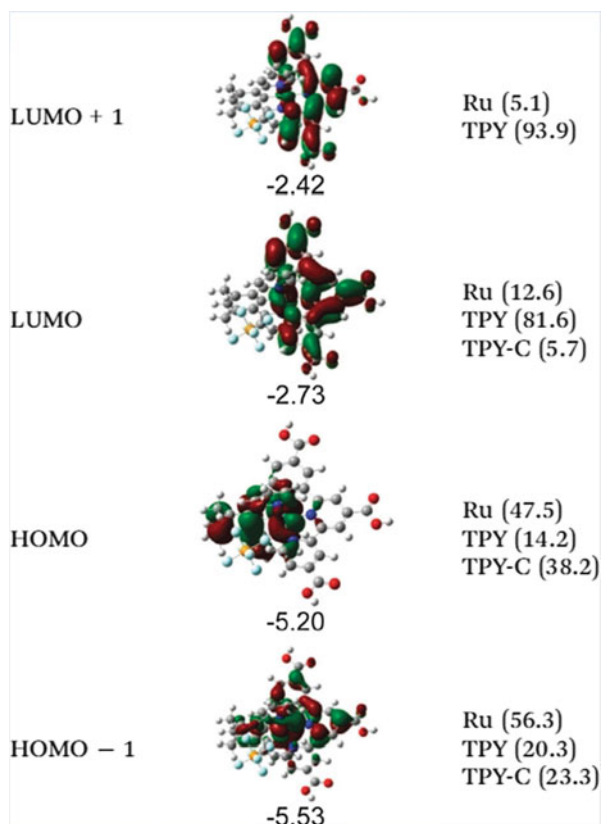


Fig. 2.12 Frontier orbitals of the complex **M3** (Fig. 2.11), their energies in eV and molecular orbital composition (%) (Reproduced from [53] with permission of the PCCP Owner Societies)

2.13a). TD-DFT calculations on this assembly gave absorption data that were in good agreement with those measured experimentally. Interestingly, the results suggest that the complexes exhibit some degree of direct-charge transfer to TiO_2 upon excitation.

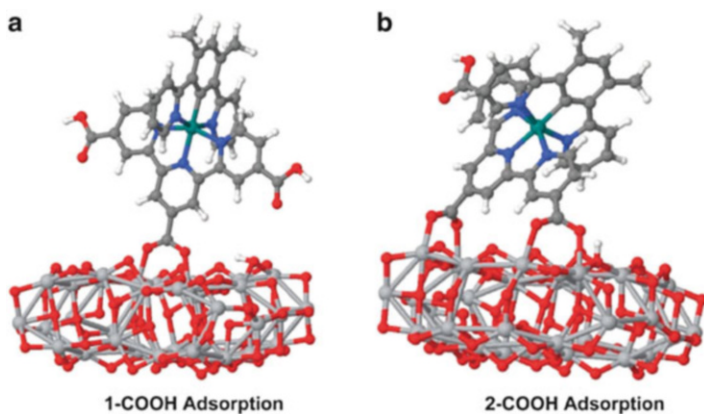


Fig. 2.13 Possible absorption configurations of the complex **M3** on $(\text{TiO}_2)_{38}$ (Reproduced from [53] with permission of the PCCP Owner Societies)

2.3.4 *Electrochemical Potentials and Interaction with the Electrolyte*

Theoretical methods are increasingly being applied to other aspects and processes involved in the DSSC. The nature of the interaction of the metal-complex dye with the redox electrolyte is of particular interest, since it determines the energetics and kinetics of dye regeneration. On the basis of experimental results, Clifford et al. proposed that dyes such as **N3** – when used in DSSCs with the I^-/I_3^- redox couple – undergo regeneration via a transient $[\text{dye}^+ - \text{iodide}]$ intermediate complex, formed by the reaction of the photogenerated dye cation with I^- [54]. Subsequent reaction with further I^- forms I_2^- . DFT methods have been applied to probe such reactions by Schreckenbach and co-workers [55] and, independently, by Privalov et al. [56]. The former authors used SDD small-core ECPs and VDZ basis sets for the halogen with solvation effects included, whilst the latter study employed a large-core ECP for iodine. Briefly, the theoretical results rule out the formation of inner-sphere, 7-coordinate $\text{Ru}(\text{II})$ species containing I^- , but do reveal that a number of outer-sphere complexes are feasible. The results also indicate that the subsequent reaction $\text{N3}^+\text{I}^- + \text{I}^- \rightarrow \text{N3I}_2^-$ is the rate-limiting step, in line with experimental conclusions.

Finally, we note that the ability to model accurate ground- and excited-state oxidation potentials of dyes for DSSCs is also clearly valuable. Excited-state oxidation potentials require accurate optimisation of the excited-state geometry. In a study on donor-acceptor triphenylamine-based organic dyes, De Angelis and co-workers have highlighted the need to use functionals with a large amount ($\sim 50\%$) of HF exchange for this purpose [57]. Such functionals are required to avoid the formation of artificial minima in twisted geometries with a high degree of charge transfer [58]. It is likely that the conclusions of this study will be equally applicable to many metal-based dyes.

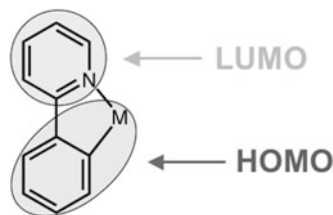
2.4 Emission Properties of Metal Complexes

Phosphorescent organometallic complexes have been widely applied in the field of phosphors for organic light-emitting devices (OLEDs), including white-light OLEDs (WOLEDs) [1, 4, 59–62]. A wide range of different metals and ligands in various combinations have been synthesised and studied both in solution and in devices. Most of these synthetic targets are time consuming and potentially costly to make, such that it is often desirable to be able to predict their emissive properties prior to synthesis as well as to rationalise experimental properties in retrospect. The knowledge of the nature of excitations taking place then allows for tailored design of new complexes. For the design of a device of a specific colour, it is important to know the energy of emission. The efficiency of emission must also be considered since compounds exhibiting a very low quantum yield in solution, or no room-temperature emission, are unlikely to be viable candidates for OLED applications. DFT and TD-DFT are increasingly used to predict and rationalise these properties, selected cases of which will be given in this section with platinum-based examples, after a brief overview of the principles involved.

2.4.1 Calculation of Emission Energy

Generation of orbital plots for the $S_0 \rightarrow T_1$ excitation of a complex can be extremely informative as to the nature of the excitation. They are also useful for suggesting what effect substituent groups at certain positions of the ligand can have on the emission energy. Such calculations for organometallic complexes incorporating the arylheterocycle unit in Fig. 2.14 – common to many of the most successful phosphors – show that the HOMO is generally located primarily on the metal and cyclometallated aryl ring, with the LUMO based on the heterocyclic ring. This was illustrated for a series of iridium(III) complexes by Hay [14]. Alteration of substituents on the aryl ring will therefore typically affect the energy of the HOMO much more than the LUMO, the opposite being true of the heterocyclic ring. Naturally, the observed effect will differ according to different positions of substitution within the rings, particularly at the 5-position where conjugation through the two rings may affect both frontier orbitals [63].

Fig. 2.14 Schematic diagram of the typical location of the frontier orbitals in cyclometallated arylpyridine complexes {e.g. where M = Ir(III) or Pt(II)}



Electron-withdrawing groups usually stabilise molecular orbitals whilst electron-donating substituents cause destabilisation. Knowledge of the position of the frontier orbitals, which can be derived from TD-DFT calculations, therefore allows control over the energy of emission obtained. For example, a compound with a higher energy of emission could be produced by addition of an electron-withdrawing group to the HOMO and/or an electron-donating group to the LUMO (a redshift is achieved by the reverse) [64]. Whilst excitation energies themselves can be produced by TD-DFT calculations, orbital plots are often more informative since they allow deliberate design of complexes tuned towards a particular wavelength of emission. Where excitation energies can be adversely affected by triplet instabilities leading to an incorrect emission energy (*vide supra*), orbital plots often provide a more reliable – albeit qualitative – way to predict how the HOMO and LUMO will be affected by various substituent groups.

The emission of light accompanying the $T_1 \rightarrow S_0$ transition does not usually involve purely HOMO and LUMO orbitals, but is rather made up of many small contributions from various other orbitals. For this reason, when considering orbital plots, those plots with the highest contribution to the excitation are normally presented alongside an indication as to the degree of their involvement. Alternatively, density difference plots can be used, which are generated by considering all the transitions, combining them and taking occupied from unoccupied to give an idea of the net movement of the electron upon excitation. Some examples follow in subsequent sections.

2.4.2 Efficiency of Emission

Experimentally, the efficiency of a compound's luminescence is measured by its quantum yield Φ_{lum} . This is determined by the relative rate constants for radiative (k_r) and non-radiative (Σk_{nr}) decay, as outlined in Equation 3 (where n_E is the number of photons emitted and n_A is the number absorbed), assuming that the emitting state is formed with unitary efficiency upon the absorption of light:

$$\Phi_{\text{lum}} = \frac{n_E}{n_A} = \frac{k_r}{k_r + \Sigma k_{\text{nr}}}. \quad (2.4)$$

In contrast to many purely organic molecules, for complexes with small ligands and metals with high spin-orbit coupling (SOC) constants, intersystem crossing is much faster than the rate of emission from the singlet excited state. Any observed emission will then normally emanate from the triplet excited state, giving phosphorescence. The exception to this rule of thumb is if the excited state is isolated away from the metal centre (e.g. when 'extended' ligands are used) [65–67].

Equation 2.4 makes clear that luminescence can be promoted either by increasing the rate of radiative decay or decreasing the rate of non-radiative decay. In phosphorescent metal complexes, the degree of metal character in the excited state becomes important in determining the efficiency of emission through its effect on

k_r , since it is thanks to the SOC effect of the metal that the spin selection rule is relaxed to promote triplet radiative decay. The rate constant for radiative decay will therefore normally be higher for excited states comprising significant metal character. Meanwhile, the Franck-Condon principle states that transitions with a high degree of orbital overlap will be more favourable than those with a lower degree of overlap, thus proceeding at an increased rate [68, 69].

Non-radiative decay of the excited states of organometallic complexes can occur through a number of different routes. The ‘energy gap law’ states that as the excited-state energy decreases (within a series of structurally similar compounds having a mutually common type of excited state), the rate of non-radiative decay of an excited-state complex will increase exponentially through intramolecular energy transfer into vibrations [70, 71]. Geometrical distortion of a compound in the excited state relative to the ground state also facilitates non-radiative decay, as illustrated schematically in Fig. 2.15. Diagram (a) illustrates the case where there is little or no distortion between the S_0 ground state and the T_1 excited state and (b) that where there is a large degree of distortion between the two states. Where there is no distortion, relaxation of the excited state to the ground state results in the emission of light (unless there is some other deactivating process). In (b), the excited-state PES is shifted with respect to that of the ground state, giving a crossing point between the two curves through which non-radiative decay can occur.

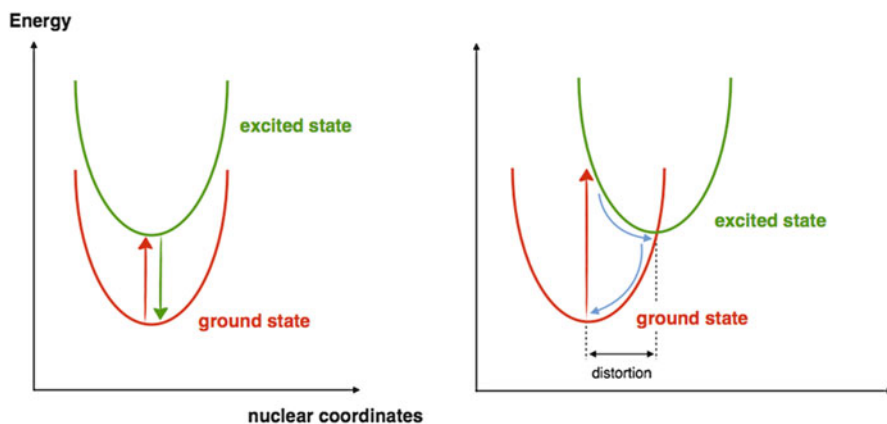


Fig. 2.15 Simplified schematic diagram highlighting how non-radiative decay is facilitated by distortion in the excited state

2.4.3 Selected Examples for Electrical-to-Light Energy Conversion (OLEDs)

2.4.3.1 Energy of Emission

A recent example of the utility of TD-DFT for understanding emission energies is provided by the work of Nisic et al. on a pair of isomeric, styryl-appended Pt (II) complexes (Fig. 2.16) [72]. It was found that irradiation of the complex with UV light resulted in isomerisation of the *trans* (E) isomer to the *cis* (Z), a process which was accompanied by a dramatic change in the absorptive and emissive properties. Whilst the *trans* isomer was non-emissive at room temperature with weak red emission at 77 K ($\lambda_{\text{max}} = 634$ nm), the *cis* showed bright green room-temperature emission. The analysis by TD-DFT (at the DFT-optimised T_1 geometry in each case) showed a marked difference in the density difference plots of the $S_0 \rightarrow T_1$ excitation between the two isomers. Whilst the *cis* isomer showed almost no involvement of the pendant group in the excitation – and indeed displays emission very much like that of the parent unsubstituted complex [73] – the plots

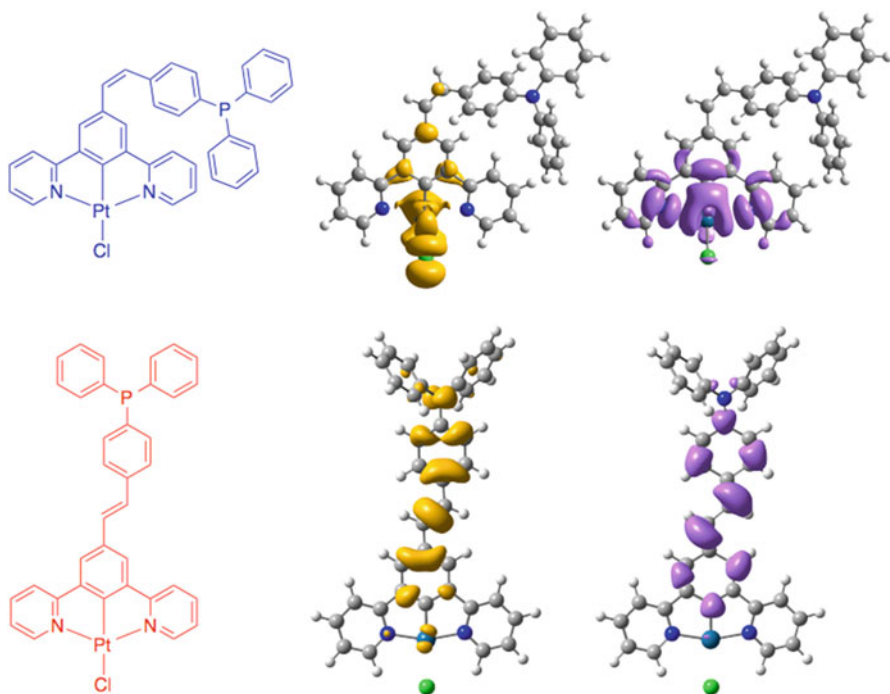


Fig. 2.16 Structures of the *cis* (top) and *trans* (bottom) isomers of the platinum complex studied by Nisic et al. [72]. Density difference plots for the $S_0 \rightarrow T_1$ transition are shown at the T_1 geometry, calculated by TD-DFT, using PBE0 in DCM. Published by The Royal Society of Chemistry

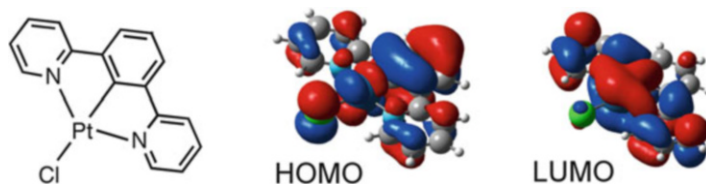


Fig. 2.17 Frontier orbitals for the Pt(II) complex of 1,3-di(2-pyridyl)benzene obtained using B3LYP and a PCM for dichloromethane solvent

for the *trans* isomer show that the movement of electron density is predominantly confined within the organic pendant itself (Fig. 2.16). Moreover, it is visually apparent from the plots that the amount of metal character in the excited state of the *trans* isomer is smaller than in the *cis*, providing an intuitively reasonable explanation for the former's low efficiency of emission.

As previously discussed, knowledge of the location of frontier orbitals allows for the rational targeting of an emission energy and hence colour: electron-donating groups destabilise molecular orbitals, whilst electron-withdrawing groups stabilise them. Farley et al. reported the synthesis and TD-DFT studies of the platinum (II) complex of 1,3-di(2-pyridyl)benzene and substituted derivatives (Fig. 2.17) [74]. The frontier orbitals generated by TD-DFT clearly show that the 4-position of the phenyl ring plays a large role in the HOMO, but almost none in the LUMO [75], and indeed, increasingly electron-donating substituents at this position increasingly redshift the emission. The reverse is true of the 4-positions of the pyridyl rings, which show involvement in the LUMO but not in the HOMO. Experimentally, electron-donating groups at these positions were found to *blueshift* the emission, in line with the prediction [64]. Overall, by judicious choice of substituents at both of these positions, the emission maxima in these systems can be tuned very simply over a wide range from about 450 to 600 nm.

2.4.3.2 Efficiency of Emission

The inclusion of spin-orbit coupling (SOC) in TD-DFT calculations is very complex and time intensive and so is not routinely attempted. Unlike singlet-singlet transitions, SOC is necessary when considering the oscillator strengths of phosphorescent processes since this is essentially the factor which is making the formally forbidden $T_1 \rightarrow S_0$ transition allowed. For this reason, the evaluation of k_r using TD-DFT remains far from routine. Tong and Che employed some of these techniques in an attempt to understand the emission efficiencies of the five Pt (II) complexes shown in Fig. 2.18 [15]. Experimental studies have shown that C[^]N[^]C-coordinated Pt(II) complexes are generally weakly emissive at room temperature and N[^]N[^]C analogues are moderately emissive, whereas N[^]C[^]N-coordinated isomers are often highly intense emitters. The experimental quantum yields for the five compounds are included in Fig. 2.18 [74, 76, 77]. Tong and Che

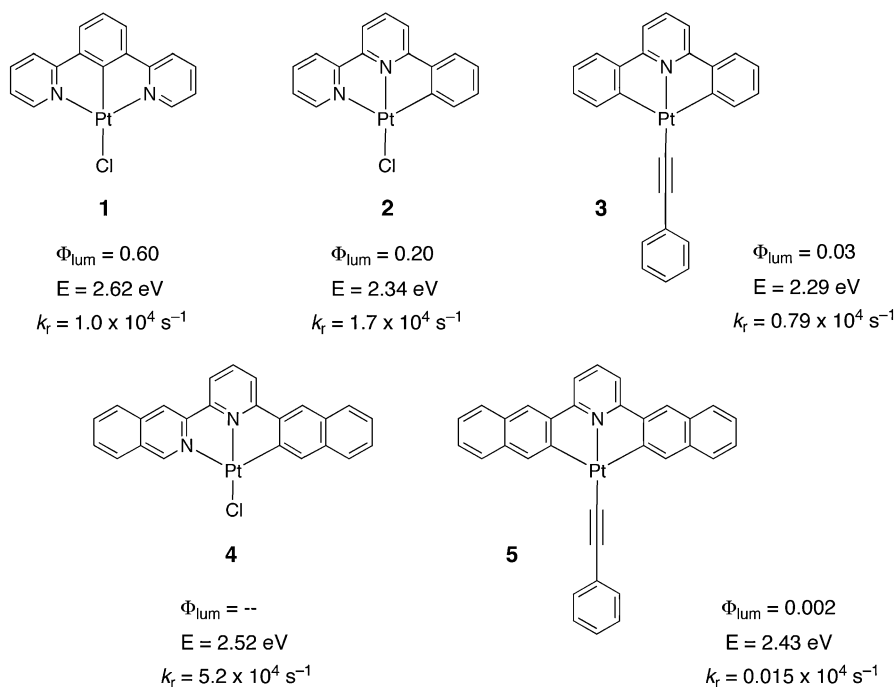


Fig. 2.18 Structures of the complexes studied by Tong and Che, together with experimental quantum yields Φ_{lum} , calculated phosphorescence energies E (in DCM) and calculated rate of radiative decay k_r for the $T_1 \rightarrow S_0$ process

sought to calculate the rates of radiative decay by looking at a combination of three factors: (1) SOC matrix elements between the emissive triplet and singlet excited states, (2) the energy ratio between those two states and (3) the oscillator strength of the $S_n \rightarrow S_0$ transition with which the emissive triplet state undergoes SOC. The value of k_r calculated for each complex is shown in Fig. 2.18. For compounds **2**, **3** and **5**, the calculated values for k_r correlate with the experiment, whereas **1** is a better emitter than expected on the basis of the calculated k_r . The authors reasoned that the emission from **1** was instead emanating from the T_2 state since k_r was much larger for that transition ($109 \times 10^4 \text{ s}^{-1}$) and the Stokes shift for the $S_0 \rightarrow T_2$ excitation at the T_1 optimised geometry was more like the value obtained experimentally than for the $S_0 \rightarrow T_1$ excitation. Consideration of the excited-state geometries of compounds **2** and **3** showed that these compounds undergo significant distortion at the T_1 excited state, suggesting efficient non-radiative decay. The complexity of considering d-orbital splittings was also underlined in this study, which described how a compromise must be made between the need for large splitting between occupied and unoccupied d-orbitals necessary to make deactivating d-d excited states thermally inaccessible and the need for occupied d-orbitals to be close in energy for efficient SOC [15].

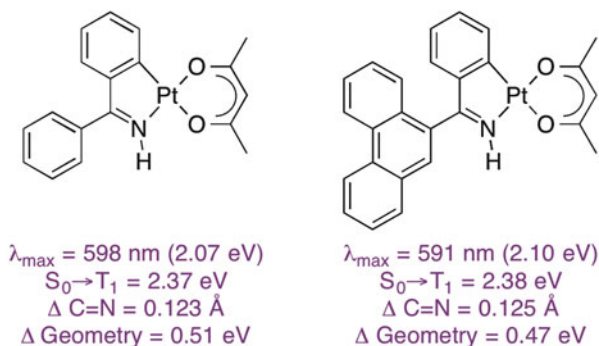


Fig. 2.19 Structures and properties of two imine-based $\text{N}^{\wedge}\text{C}$ -coordinated Pt(II) complexes studied by Pandya et al. $\lambda_{\max}$ represent the experimentally measured emission in DCM at 298 K, $S_0 \rightarrow T_1$ the calculated excitation energy at the ground-state geometry, $\Delta \text{C=N}$ the change in the C=N bond length between the S_0 and T_1 geometries and Δ geometry the difference between the energy of the ground state at the S_0 geometry and the single-point energy at the T_1 geometry

The influence of excited-state distortion has also been considered for a series of Pt(II) complexes with imine-based $\text{N}^{\wedge}\text{C}$ -coordinating ligands, of which two examples are shown in Fig. 2.19 [78]. Both complexes showed almost no emission in solution at 298 K, despite the structural resemblance to numerous successful emitters such as $\text{Pt}(\text{N}^{\wedge}\text{C-ppy})(\text{acac})$. DFT and TD-DFT calculations were employed in an attempt to rationalise the processes taking place that result in such efficient non-radiative deactivation of the excited state. The $S_0 \rightarrow T_1$ excitation energy at the S_0 and T_1 geometries was calculated. These showed very different energies from those obtained experimentally, suggesting that the T_1 excited-state geometries were very different from the ground-state geometries. The calculated T_1 geometry revealed that the C=N bond is substantially elongated compared to the ground state. It was also noted that single-point singlet calculations at the T_1 geometry gave quite different SCF energies from the values calculated at the ground-state geometries (Fig. 2.19), which again points to excited-state distortion. The application of this technique does, however, rely heavily on small differences in computed energies and so should be approached with some caution: inherent errors of up to about 0.3 eV are considered quite normal for TD-DFT work, and the presence of triplet stabilities can lead to a detrimental effect on the accuracy of triplet-state energies.

The synthesis, liquid crystal and luminescent properties of a series of ortho-platinated complexes incorporating $\text{N}^{\wedge}\text{C}$ -coordinated arylpyridines in conjunction with β -diketonate ligands have been reported by Spencer et al. [79]. Such complexes (i.e. those of the form $[\text{Pt}(\text{N}^{\wedge}\text{C})(\text{O}^{\wedge}\text{O})]$) generally form a lowest triplet excited state located on the metal and cyclometallated ligand (as in Fig. 2.14), with the diketonate acting as an ‘innocent’ ancillary ligand, with little effect on the emission properties. However, it was observed that, in this instance, whilst $\text{Pt}(\text{ppy})(\text{acac})$ displayed the expected phosphorescence in solution at room temperature, $\text{Pt}(\text{ppy})(\text{hfac})$ showed no emission under the same conditions (the structures are shown in Fig. 2.20). Moreover, two isomers of the tfac complex were formed, of

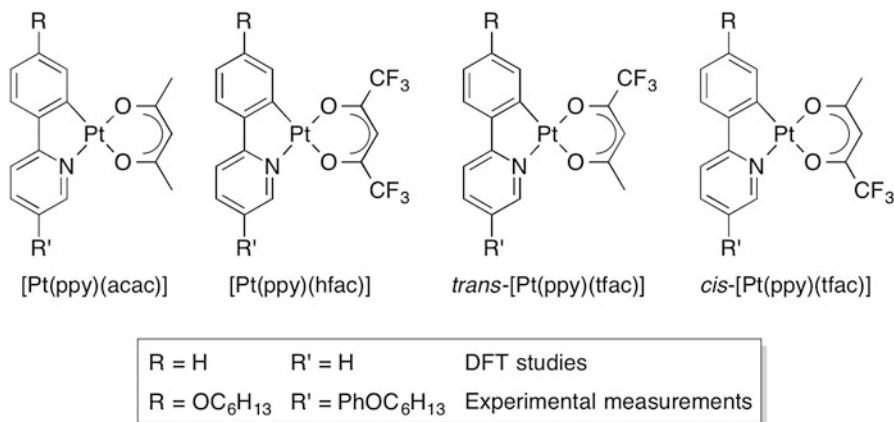


Fig. 2.20 The structures of the four Pt(N[^]C)(O[^]O) complexes studied by Spencer et al. [79]

which the *trans* isomer emits at a higher energy than the *cis*, but with a significantly lower quantum yield (here, *trans/cis* refers to the relative disposition of the CF₃ group and the pyridyl ring). *S*₀ ground-state geometries of the four complexes were optimised using DFT, and the density difference plots for the *S*₀ → *T*₁ excitation of each complex at this geometry are shown in Fig. 2.21. It can be seen that the non-emissive Pt(ppy)(hfac) shows a marked difference from the other three compounds. Its density difference plot involves electron depletion from the aryl ring of the ppy ligand and augmentation on the hfac ligand. In contrast, the other three complexes display rearrangement of electron density on the ppy ligand upon excitation, in line with excited states normally calculated in Pt(N[^]C)(O[^]O) complexes, i.e. *d*_{Pt} / π_{N[^]C} → π*_{N[^]C}. The change in excitation shown for Pt(ppy)(hfac) was attributed to the stabilisation of the orbitals by the electron-withdrawing CF₃ groups to such an extent that the LUMO is positioned on the O[^]O ligand instead. It was also shown that this excitation has a lower orbital overlap, showing that the reduced quantum yield could – at least in part – be due to a lower rate of radiative decay.

Moreover, by evaluating the first triplet excited-state geometry (*T*₁) of each of the four complexes, the researchers revealed another likely contribution to the variation of emission efficiency amongst the four complexes. The comparison of the *S*₀ and *T*₁ geometries (both calculated by DFT) for each of the four complexes shows more significant excited-state distortion for some complexes than others. Figure 2.22 shows the *T*₁ geometry of each complex superimposed upon its respective ground-state geometry, *S*₀. Whilst Pt(ppy)(acac) undergoes virtually no geometrical distortion upon excitation, all of the other three complexes do so, to varying degrees. The largest change in geometry is shown by Pt(ppy)(hfac). The significant distortion in the hfac complex is a likely reason for the increase in non-radiative decay, which, combined with a decrease in radiative decay noted above, accounts for the lack of emission displayed by this complex. Similar reasoning may explain the difference in emission efficiencies between *cis*- and

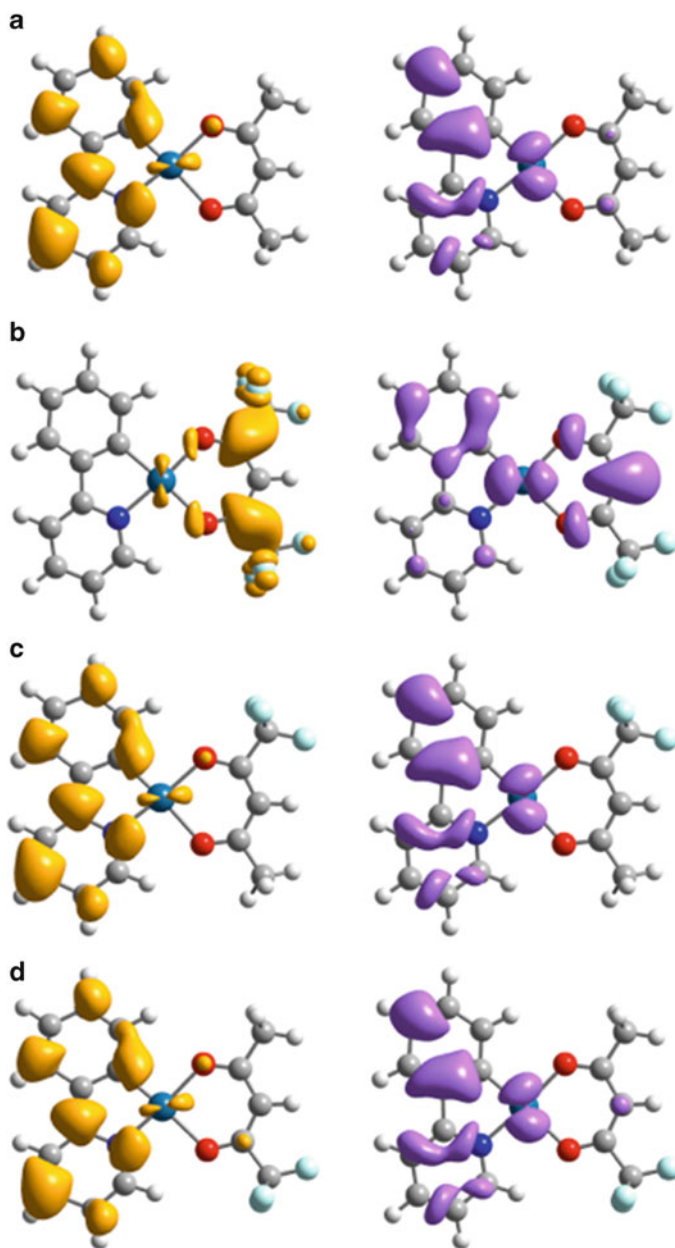


Fig. 2.21 Density difference plots for the $S_0 \rightarrow T_1$ excitation of the four complexes of Fig. 2.20 at the ground-state geometry: (a) Pt(ppy)(acac), (b) Pt(ppy)(hfac), (c) *trans*-Pt(ppy)(tfac) and (d) *cis*-Pt(ppy)(tfac). Electron depletion shown on the *left* and accretion on the *right* (Reproduced from [79] with permission from The Royal Society of Chemistry)

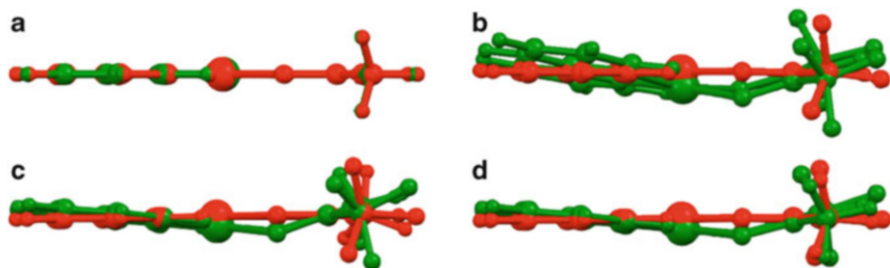


Fig. 2.22 Superimposed structures of the S_0 ground state (planar) and T_1 excited state (distorted) for the complexes of Fig. 2.21: (a) Pt(ppy)(acac), (b) Pt(ppy)(hfac), (c) *trans*-Pt(ppy)(tfac) and (d) *cis*-Pt(ppy)(tfac) (Reproduced from [79] with permission from The Royal Society of Chemistry)

trans-Pt(ppy)(tfac). The quantification of the extent of distortion by calculation of the root-mean-square displacement of the atoms between the two states (S_0 and T_1) shows that the extent of distortion increases in the order:

$$[\text{Pt(ppy)(acac)}] < \textit{cis}\text{-}[\text{Pt(ppy)(tfac)}] < \textit{trans}\text{-}[\text{Pt(ppy)(tfac)}] \\ < [\text{Pt(ppy)(hfac)}].$$

Greater distortion in the T_1 state of the *trans* isomer compared to the *cis* may lead to a greater rate of non-radiative decay and thus to the observed less efficient emission at room temperature.

2.5 Conclusions

In this short contribution, we have sought to provide an indication of how theoretical methods based on density functional theory are being increasingly used to probe ground- and excited-state properties of metal complexes relevant to their use in energy conversion. Early work in this area at the beginning of the century tended to focus primarily on using TD-DFT to obtain qualitative information about trends in absorption energies and the orbital parentage of lowest-lying excited states. More recently, studies have expanded to consider more explicitly factors such as triplet states, phosphorescence, effect of solvent, structural distortion in the excited states compared to the ground state and immobilisation of complexes onto semiconductors, to name but a few.

There remain major challenges: methods are still mostly used retrospectively to rationalise behaviour and rarely to predict properties in advance of synthesis. In particular, being able to predict the efficiency of emission is a complicated problem: a detailed analysis would require a full treatment of spin-orbit coupling pathways and evaluation of the coupling mechanisms between excited electronic states and all vibrational modes – utterly unfeasible for molecules of this size. Nevertheless,

by using simple concepts such as those relating deactivation pathways to the degree of structural distortion in the excited state, valuable deductions can be made.

As far as excited-state energies are concerned, there is often a good agreement between theory and experiment for singlet states, and many studies have been able to show a satisfactory match between experimental absorption spectra and those simulated using TD-DFT. On the other hand, the analysis of emission is much less common, as it requires knowledge of the relaxed excited-state geometry. For phosphorescence from the triplet state, the situation should be aided by the fact that DFT can be used to directly determine the lowest state of any multiplicity, thus including the T_1 . But triplet instabilities can cause unexpected problems, particularly in those excited states which have high orbital overlap. The recent implementation of the Tamm-Dancoff approximation into some of the commercial DFT packages is likely to go some ways to dealing with these issues.

Clearly, the continual development of new and improved functionals and basis sets, as well as faster computer power, renders the area one which is bound to enjoy major advances over the next decade.

Acknowledgements We thank our colleagues Prof David Tozer (Durham University) and Dr Michael Peach (University of Lancaster) for stimulating discussions and collaborative work on theory applied to excited states of metal complexes. Our work in the field has been supported by a studentship from EPSRC (to G.R.F., grant ref. EP/G06928X/1) and facilitated by Durham University through access to its high-performance computing facility.

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Organometallics and Related Molecules for Energy
Conversion

Wong, W.-Y. (Ed.)

2015, XIII, 537 p. 378 illus., 125 illus. in color.,

Hardcover

ISBN: 978-3-662-46053-5