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Dye Chemistry with Time-Dependent Density Functional Theory

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In this perspective, we present an overview of the determinations of excited-state properties of "real-life" dyes, and notably of the optical absorption and emission spectra, performed during the last decade with Time-Dependent Density Functional Theory (TD-DFT). We discuss the results obtained with both vertical and adiabatic (vibronic) approximations, choosing relevant examples for several series of dyes. These examples include, reproducing absorption wavelengths of numerous families of coloured molecules, understanding of the specific band shape of amino-anthraquinones, optimising the properties of dyes used in solar cells, mimicking the fluorescence wavelengths of fluorescent brighteners and BODIPY dyes, studying optically-active biomolecules and photo-induced proton transfer, as well as improving the properties of photochromes.

1 Introduction

Dye chemistry is one of the key research domain that has stimulated the rapid development of chemical sciences in the late nineteen century. Indeed, the economical interest to industrially produce large quantities of dyes dates back from that time. Amongst the earliest synthesis of coloured compounds, one could certainly point out the discovery of mauvein, the first artificial dye by Perkin,[1] as well as the works of von Baeyer devoted to indigo.[2] Clearly, the original economic goal was to obtain dyes from synthesis rather than plant extraction. This was an astonishing success, e.g., the synthesis of alizarin (1,2-OH-9,10-anthraquinone) a red compound that was originally extracted from madder (*Rubia tinctorum*), rapidly led to the collapse of the madder market, and hence of the agricultural regions producing this plant. This fierce *dye rush* can be illustrated by the fact that patents related to the synthesis of alizarin were filled within one day by English (Perkin) and German (Graebe and Liebermann) chemists. Relatively rapidly, the rational development of new (non-naturally known) dyes became the focus of many experimental investigations, and, consequently, the *a priori* predictions of the colour, or more specifically of the longest wavelength of maximal absorption (λ_{max}), became a prized goal. Experimentally, dye design can be performed by synthesising a series of molecules with limited chemical variations, so to identify the chromophore and

to appraise the impact of various secondary groups (so-called auxochromes). During the sixties, this task was performed by Luttke and collaborators for indigo, and it allowed identifying the H-shaped indigoid chromophore, but it implied very intense experimental efforts.[3–5] The first theoretical methods to predict λ_{max} relied on tables listing empirical (and incremental) auxochromic effects, determined from known spectral measurements obtained for the most important classes of chromogens. A very good example of this approach was proposed by Labhart in 1957 for anthraquinones.[6] However, such scheme is inherently limited because it cannot deal with unknown auxochromes nor new chromophoric core. The second widely popular approach was the ZINDO model (Zerner's Intermediate Neglect of Differential Overlap), a semi-empirical method specifically parametrized to reproduce UV/Vis signatures.[7] ZINDO is very successful for several families of coloured molecules (e.g., methylene blue, coumarins, etc.)[8,9] but can be rather poor for simple dyes (e.g., anthraquinones)[10] and even fails miserably for indigo derivatives.[11,12] Though ZINDO is an ultra-fast method on modern computer architectures, the obtained accuracy can hardly be crystal-balled, and some alternative semi-empirical approaches have been proposed to quickly reach more consistent estimates of the experimental λ_{max}, although fine tuning of the parameters is often required.[13,14]

During the last three scores, the emergence of powerful *ab initio* methods allowed to probe more accurately the electronically excited states of conjugated molecules. On top of the CIS (Configuration Interaction Singles) method[15] that delivers an accuracy for excited-states (ES) comparable to Hartree-Fock (HF) for the ground states (GS), that is, hardly satisfying, one can split these *ab initio* approaches into two categories: wavefunction-based methods and density-based schemes. In the former category, one first finds the CAS-SCF (Complete

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Active Space Self Consistent Field) approach,[16] that has often been applied to investigate photochemical reactions, but is not the most suited scheme for accurately simulating the spectral signatures as the dynamical correlation is not accounted for. Next, one has a series of highly-correlated schemes, e.g., CAS-PT2 (CAS second-order Perturbation Theory),[17] MR-CI (Multi-Reference CI),[18] EOM-CC (Equation-of-Motion Coupled Cluster)[19,20], ADC (Algebraic Diagrammatic Construction),[21] SAC-CI (Symmetry Adapted Cluster CI),[22] etc. and all these approaches generally yield accurate data particularly for the challenging doubly-excited states and open-shell molecules but at a computational cost impeding applications on a large set of molecules due to unfavourable scaling.[23] The most affordable method of the wavefunction series, CC2, can be used to model medium-sized compounds (ca. 50 atoms), but the obtained absolute accuracy remains a matter of debate in the literature, though it is recognised that CC2 restores the chemical trends very satisfactorily in most cases.[24–34] The extension of the GS Density Functional Theory (DFT) to the ES, Time-Dependent DFT (TD-DFT), has the advantage to be a formally exact theory,[35] and Casida provided exact expression for calculating the excitation energies.[36] The vast majority of TD-DFT's applications require two approximations: on the one hand, the adiabatic approximation (that is considering frequency-independent exchange and correlation kernel, which induces a loss of memory effects) and, on the other hand, the choice of an adequate exchange-correlation functional.[37] In the series of available methods used for ES simulations, we also wish to highlight the GW[38,39] and the Bethe-Salpeter (BSE)[40,41] Green's function many-body perturbation theories, that can be viewed as an extension of both HF or DFT methods. GW and BSE have become increasingly popular in the chemical community during the last few years, and several convincing applications on both small and medium sized molecules appeared,[42–47] though it is probably too early to assess the *pros* and *cons* of these two methods in the framework of dye chemistry. Indeed, up to now, the BSE method has provided an accuracy for organic dyes similar to the one obtained with carefully performed TD-DFT calculation.

Despite the two above-mentioned limits, TD-DFT clearly remains the most applied theory for evaluating the spectral properties of medium and large dyes (ca. 1000 papers in 2013, one order of magnitude above CC2, for instance). This popularity can be traced back to: i) the simplicity of this single-reference method,[48] that does not imply complex or system-dependent inputs; ii) the speed of the computations, chemicals with ca. 3000 basis functions can be treated routinely even when hybrid functionals are used,[49] and even larger systems can be tackled if simplified schemes are applied;[50] iii) the availability of both analytic first (gradients)[51–53] and second (Hessian) derivatives[54,55] making the exploration of the ES potential energy surface (PES) possible on a systematic

basis, consequently allowing to efficiently model fluorescence spectra and vibronic couplings; iv) the possibility to couple TD-DFT with a series of environmental model, applicable for solvents,[56–61] biomolecules,[62–65] cages,[66,67] metals[68] and solids[69–71] (for a specific discussion about environmental effects and TD-DFT, we redirect the reader to our 2011 PCCP perspective article).[72] All together, these advances allow tackling complex chemical problems -though in an approximate way- and this includes modern dye chemistry challenges, e.g., designing compounds with large Stokes shifts through excited-state intramolecular proton transfer (ESIPT), enhancing the light harvesting character of dyes used in DSSC (Dye-Sensitised Solar Cells), producing white emitting organic diodes, optimising the contrast in multiphotochromic molecules, finding new probes for pollutants, boosting the properties of fluorescent proteins and tuning the FRET (Fluorescence Resonance Energy Transfer).

In this perspective, we do not intend to discuss the fundamentals of TD-DFT, a subject tackled in several excellent books, reviews, tutorials and perspectives previously,[23,48,69,72–93] nor to present alternatives to the LR-TD-DFT model, e.g., spin-flip, dressed or constricted variational approaches,[94–102] nor to propose the selection of appropriate exchange-correlation functionals, a subject that requires the analysis of large TD-DFT benchmarks, a topic recently reviewed by us.[37] Indeed, our focus here will be set on the applications of the "standard" TD-DFT model to solve different aspects of dye chemistry problems. For this reason, this perspective is split in terms of chemical cases and their applications and is not divided by level of theories. Nevertheless, the next Section provides a brief overview of the main approaches used.

2 Methodological overview

The comparisons of experimental and theoretical absorption and emission spectra of real-life structure is not straightforward, as one should model, not only the transition energy from the GS to a given ES, but also its probability (oscillator strength), and more importantly the overlap between the vibrational wavefunction of the two electronic states. In that framework, one could state that the properties allowing meaningful comparisons between measurements and simulations are, on the one hand, the vibrationally resolved band shapes, and, on the other hand, the so-called 0-0 energies (E^{0-0}, see Figure 1). The former can be obtained by the computation of Franck-Condon (and/or Herzberg-Teller) factors -at least in the harmonic approximation[103–111] whereas it is admitted that the latter can be compared to the crossing point between absorption and fluorescence bands (AFCP).[31,112,113] E^{0-0} corresponds to the difference between ES and GS energies at their respective

minima, corrected for zero-point vibrational energies (ZPVE):

$$E^{0-0} = E^{\text{adia}} + \Delta E^{\text{ZPVE}} \tag{1}$$

$$E^{\text{adia}} = E^{\text{ES}}(R^{\text{ES}}) - E^{\text{GS}}(R^{\text{GS}}) \tag{2}$$

$$\Delta E^{\text{ZPVE}} = E^{\text{ZPVE}}(R^{\text{ES}}) - E^{\text{ZPVE}}(R^{\text{GS}}) \tag{3}$$

Obviously, these two comparisons involve the determination of the ES vibrational frequencies, and are therefore costly in terms of computational resources. Indeed, in practice, it becomes almost technically impossible to compute ΔE^{ZPVE} for compounds containing more than 150 atoms using a full TD-DFT approach in gas phase or with implicit solvent. For this reason, and, due to the non availability of analytical TD-DFT derivatives in widely available codes prior to ca. 2008, many works have focussed on the vertical absorption energies, that do not require the exploration of the ES geometry,

$$E^{\text{vert-abso}} = E^{\text{ES}}(R^{\text{GS}}) - E^{\text{GS}}(R^{\text{GS}}), \tag{4}$$

For large systems, there is no reliable vertical experimental data available, so that one is left with comparisons between theoretical $E^{\text{vert-abso}}$ and experimental λ_{max}, that cannot be viewed as well-grounded. Despite, this limitation that will certainly disappoint diehard theoreticians, such approximation might be useful for dye design, as, in an homologous series of structures. Indeed, one can often consider the geometric and vibrational relaxation as constant, so that auxochromic shifts can be computed rapidly and efficiently within the vertical approximation.
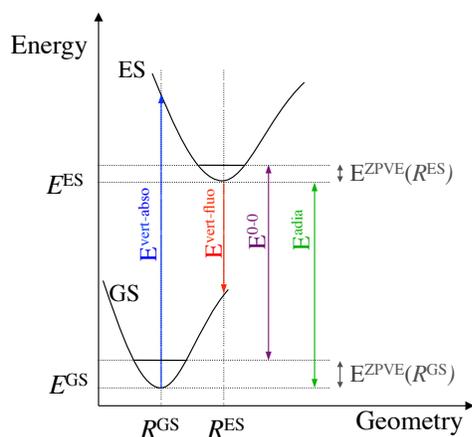
Fig. 1 Simplified potential energy curve diagram representing only two singlet states free of intersections. Adapted with permissions from D. Jacquemin, A. Planchat, C. Adamo, B. Mennucci J. Chem. Theory Comput. 2012, **8**, 2359–2372. Copyright 2012, American Chemical Society.

For fluorescence, one can of course limit the investigation to the vertical contribution,

$$E^{\text{vert-fluo}} = E^{\text{ES}}(R^{\text{ES}}) - E^{\text{GS}}(R^{\text{ES}}) \tag{5}$$

but it nevertheless requires the optimisation of the ES structure, a task possible up to ca. 250 atoms.[114] These calculations can be fast and allow estimating the Stokes shift (Δ^{SS}) by a simple difference with the vertical absorption data. This is efficient but completely neglects vibrational effects.

Although most examples treated herein are related to organic dyes, it is certainly worth to mention that for compounds containing heavy atoms, relativistic (spin-orbit) effects might significantly affect both absorption and emission spectra and should therefore been accounted for.[115,116]

When the dye is embedded in an environment, it is important to determine how the medium is reacting to the change of electronic state of the chromophore. Irrespective of the environmental model, one often distinguishes the non-equilibrium and the equilibrium regimes. In the former, only the electrons of the surroundings do react to the change of the chromophore, the nuclei being frozen. This is adequate for fast phenomena (absorption and fluorescence). In the latter regime, a full relaxation (both electrons and nuclei) takes place, an approach adapted to optimise the geometry of the ES.[117] Modelling the spectroscopic properties of dyes in a complex environment such as solvent, proteins, DNA or even membranes is of prime importance to compare theoretical results with experiment for "real-life" cases. Implicit models such as the Polarisable Continuum Model (PCM) of Tomasi and coworkers,[117] Truhlar's Solvent Models (SMx)[118] and the three-dimensional Reference Interaction Site Model (3D-RISM)[119,120] are widely used in the dye community for their great efficiency and ease of use. They can be applied to account for solvatochromic effects or even to crudely reproduce a protein medium. Actually, many results presented in this perspective rely on such implicit models that are also known to present two major drawbacks: i) the specific interactions between the dye and its surroundings are (mostly) neglected; and ii) the surrounding is considered to be uniform and isotropic. Therefore for some solvated dyes, e.g., when considering a protic solvent, solute-solvent proton transfers..., it is more valuable to account for explicit solvent molecules lying within the first solvation shell which are surrounded by an implicit model. Within a more complex scale such as a probe into a protein/DNA matrix, it is obvious that both the absorption and emission of the chromophore are highly sensitive to the variation of its local environment. The heterogeneity has therefore to be modelled with careful attention as implicit models typically yield poor results. We however point out that a formulation of the IEF-PCM model has been developed to describe the heterogeneity of a lipid bilayer using a position dependent permittivity.[121] Nevertheless, for complex environments, reasonable and convenient schemes are hybrid quantum mechanics and molecular mechanics (QM/MM) methods. A large panel of schemes exist in the literature and they differ by the QM/MM cutting procedure and/or the selected MM method.[122] Basi-

cally the chromophore and some of its nearest neighbouring residues/molecules are described using TD-DFT and the rest of the system (cage, protein, enzyme, DNA...) is represented using a force field. While, for a rather long time, only the mechanical and electrostatic embeddings were considered, more recently many efforts have been directed towards the development of polarisable force field explicitly accounting for the polarisation embedding, i.e., when a chromophore absorbs light, the electronic response of surrounding can be included. These QM/MM methods are now frequently used to model dyes embedded into a macromolecule. Of course, effects related to structural variations due to thermal disorder are also of importance and dynamical simulations are often a preliminary step.

3 Colour Chemistry

Without doubts, the main application of dyes in terms of industrial impact remains the production of coloured materials, through absorption of the incoming photons and observation of the reflected or transmitted light. In this field, one generally classifies the molecules either by dyeing process (vat, acid, direct, disperse, etc. dyes) or chemical family.[123–129] In Table 1, we collected a series of theoretical vertical TD-DFT works following this second classification. Our selection was made considering several factors, e.g., the industrial importance of the studied family, the number of molecules considered, the level of theory selected, etc. Of course, several general studies encompassing multiple series of chromophoric families are available as well.[11,130–135] Note that the relatively small number of inorganic or metal-containing structures listed in Table 1 is the consequence of the dual difficulty to obtain a large set of consistent experimental measurements performed on closely related inorganic structures, and the challenge of analysing experimental spectra that often present overlapping bands, making the use of a convolution procedure a prerequisite.[136] Consequently, most TD-DFT studies dealing with inorganic dyes treated a rather small number of chemically-relevant cases, rather than a statistically significant number of dyes.[137–143]

In terms of methodology, one notices in Table 1 a clear domination of B3LYP[203,204] and PBE0[205,206] calculations, and this is due, not only to the early availability of these hybrid exchange-correlation functionals in many quantum chemical packages, but also to their ability to produce reasonably accurate data in the vertical model.[132,133] Nevertheless, if most of the errors reported in Table 1 are quite small (several below 0.1 eV), this should not be viewed as an empirical proof of the validity of the vertical TD-DFT approximation, but more as the illustration that a careful selection of a specific exchange-correlation functional can yield extremely satisfying estimates. Indeed, several of the listed works implied an initial methodological assessment in order to pinpoint the

most adequate functional/basis set combination. However, two types of problematic states emerge: on the one hand, charge-transfer (CT) transitions and the associated spurious excited-states, a well-identified difficulty[11,207–212] that can be solved using range-separated hybrid functionals,[30,213–228] and, on the other hand, cyanine derivatives, for which TD-DFT almost systematically produces too large transition energies, a topic discussed in the literature,[229–236] but not yet fully mastered. In the following, we selected a few specific classes of dyes to illustrate the typical "colour chemistry" analysis that can be made with the TD-DFT tool, with and beyond the vertical approach.

3.1 Anthraquinones

9,10-anthraquinones are particularly versatile dyes,[125,127,128] and vertical TD-DFT investigations have been performed.[10,130,145–147,237–240] They indicated that conventional hybrid functionals, B3LYP and PBE0, provided accurate results. Indeed, for the 189 neutral derivatives of Refs 145, 146 and 240, the mean absolute error (MAE) is 0.10 eV irrespective of the use of B3LYP or PBE0. If one wishes to further refine the "raw" TD-DFT values, multiple linear regression can be a handy tool,[81]

$$\lambda_{max}^{exp} = -33.5 - \frac{848.7}{E_{B3LYP}^{vert-abso}} + \frac{2238.4}{E_{PBE0}^{vert-abso}} \qquad (6)$$

where the wavelengths are in nm and the vertical energies in eV. This equation yields a MAE of 0.08 eV and limits the number of large deviations (> 0.15 eV) to less than 15%, therefore outperforming both B3LYP and PBE0 but at the price of two TD-DFT calculations for a single dye.[81] Whilst such approach allows a rapid estimation of the position of the absorption band of unknown anthraquinone, it cannot be considered as completely satisfying, as it gives no information on the experimental band shapes, and several hydroxy- and amino-anthraquinones are known to present multiple absorption peaks in the visible domain.[125,241,242] These multiple maxima have been associated with several effects, including aggregation,[243] tautomeric equilibrium[244–246] and vibrational couplings.[247] The actual origin has been fully resolved with TD-DFT for 1,4-NH_2-9,10-anthraquinone (see representation in Figure 2).[248,249] The applied strategy was first to discard the tautomeric origin. Indeed, DFT clearly indicates that the equilibrium is strongly displaced on the keto-amine side, all possible enol-imine isomers being much less stable (ca. 0.5 eV), preventing their formation on the ground-state. On top of that, these non-canonical structures do not correspond to true minima of the ES PES, so that tautomers cannot be formed after absorption. It is nevertheless worth to note that this conclusion does not necessarily hold for anionic hydroxy-anthraquinones, for which specific tautomers may play a role in the observed

Table 1 Selected vertical TD-DFT studies performed on chromophores. We indicate the dye family, the nature of the ES considered and their number (Nb). Method indicates the functional and atomic basis set used in the TD-DFT part of the calculations. The mean absolute errors (MAE) are computed from a straightforward statistical comparison between $E^{\text{vert}-\text{abso}}$ and experimental λ_{max}, and are given in eV.

Family	Nature	Nb	Method	MAE	Ref.
Anthocyanine	$\pi \to \pi^\star$	23	B3P86/6- 311+G(d,p)	0.25	144
Anthraquinone	$\pi \to \pi^\star$	66	PBE0/6-31G(d,p)	0.09	145
	$\pi \to \pi^\star$	101	PBE0/6-31G(d,p)	0.10	146
	$\pi \to \pi^\star$	8	B3LYP/6-311++G(d,p)	0.13	147
Aza-BODIPY	Cyanine/Charge-transfer	8	BMK/6-311+G(2d,p)	0.18	148
Azobenzene	$n \to \pi^\star$ & $\pi \to \pi^\star$	187	CAM-B3LYP/6-311+G(d,p)	0.10	149
	$n \to \pi^\star$ & $\pi \to \pi^\star$	15	PBE0/TZVP	0.15	150
	$\pi \to \pi^\star$	38	B3LYP/cc-pVDZ	0.18	151
Azoalkane	$n \to \pi^\star$	24	PBE0/6-311+G(d,p)	0.06	152
Benzodifuranone	$\pi \to \pi^\star$/Charge-transfer	18	M06-2X/6-311+G(2d,p)	0.05	153
Benzylideneaniline	$\pi \to \pi^\star$	68	PBE0/6-311+G(2d,p)	0.19	154
Coumarin	$\pi \to \pi^\star$	127	PBE0/6-311+G(2d,2p)	0.18	155
	Charge-transfer	5	B3LYP/6-31+G(d,p)	0.24	156
	Charge-transfer	21	PBE0/6-31+G(d,p)	0.21	157
Croconate	Mixed valence	18	B3LYP/6-311G(d,p)^a	0.12	96
Cyclohexanone/Piperidone	$\pi \to \pi^\star$	9	B3LYP/6-31G	0.09	158
Cyanine	Cyanine	9	B3LYP/6-311G(d)	0.31	159
Diazonium Salt	$\pi \to \pi^\star$	15	PBE0/6-311G(2d,2p)	0.07	160
Diphenyleaniline	$\pi \to \pi^\star$/Charge-transfer	27	PBE0/6-311++G(2d,p)	0.06	161
Dithienylethene	$\pi \to \pi^\star$	78	Tuned-CAM-B3LYP/6-311G(d,p)	0.03	162
	$\pi \to \pi^\star$	329	PBE0/6-311+G(2d,p)	0.15	163–168^b
Epicocconone	$\pi \to \pi^\star$	17	B3LYP/6-31++G(d,p)	0.30	169
Formazan	$\pi \to \pi^\star$	10	PBE0/6-311G(2d,2p)	0.03	170
Fulgide	$\pi \to \pi^\star$	22	M06/6-311G(d,p)	0.06	171
Hydrazone	$\pi \to \pi^\star$	82	PBE0/6-311+G(2d,p)	0.12	172
Indigo	$\pi \to \pi^\star$	86	B3LYP/6-311+G(2d,p)	0.02	12
Naphthoquinone	$\pi \to \pi^\star$	69	PBE0/6-311+G(2d,p)	0.10	173
	$\pi \to \pi^\star$	151	PBE0/6-311+G(2d,p)	0.11	174
1,8-Naphthalimide	$\pi \to \pi^\star$	39	PBE0/6-31+G(d)	0.21	175
	$\pi \to \pi^\star$	23	PBE0/6-31+G(d)	0.13	176
Nitroso	$n \to \pi^\star$	22	PBE0/6-311++G(3d,3p)	0.05	177
N-methylmaleimide	$\pi \to \pi^\star$/Charge-transfer	20	B3LYP/ 6-31+G(d,p)	0.10	178
Organoboron-azole	$\pi \to \pi^\star$	12	B3LYP/6-311++G(d,p)	0.15	179
Oxazine	$\pi \to \pi^\star$/Cyanine	10	M06/6-311++G(d,p)	0.08	180
Pechmann	$\pi \to \pi^\star$	12	BMK/DGDZVP	0.12	181
	$\pi \to \pi^\star$	6	PBE0/DZVP	0.17	182
Phthalocyanine	$\pi \to \pi^\star$	6	B3LYP/6-31G(d)	0.11	183
	$\pi \to \pi^\star$	10	BP86/6-31G(d)	0.13	184
Polyphenol (flavonoid)	$\pi \to \pi^\star$	30	B3P86/6-311+G(d,p)	0.19	185
	$\pi \to \pi^\star$	9	B3LYP/6-31+G(d)	0.10	186
Porphyrin (and related)	$\pi \to \pi^\star$	7	B3LYP/6-31G(d)	0.07	187
	$\pi \to \pi^\star$	11	PBE0/6-31+G(d)	0.25	188
	$\pi \to \pi^\star$	20	PBE0/6-31+G(d)	0.23	189
Pyrene	$\pi \to \pi^\star$	43	B3LYP/cc-pVTZ	0.22	190
Pyridylazulene	$n \to \pi^\star$ & $\pi \to \pi^\star$	24	PBE0/6-311++G(2d,2p)	0.20	191
Ru/Os Polypyridyl	$\pi \to \pi^\star$/Charge-transfer	10	PBE0/6-31G(d)/CEP-121	0.11	192
	$\pi \to \pi^\star$/Charge-transfer	6	PBE0/LanL2DZ	0.12	193
Spirroxazine (open isomer)	Cyanine	25	TPSSh/6-311+G(2d,p)	0.24	194
Squaraine	Cyanine	39	BLYP/6-311G(d,p)	0.14	195
	Cyanine	13	PBE0/SVP	0.31	29
Streptopolymethine	Cyanine	7	BLYP/6-311+G(d,p)	0.64	134^c
Thienopyrazine	Charge-transfer	21	CAM-B3LYP/6-311+G(2d,p)	0.12	196
Thiocarbonyl	$n \to \pi^\star$	102	B3LYP/6-311+G(2df,p)	0.07	197
	$n \to \pi^\star$ & $\pi \to \pi^\star$	29	B3LYP/6-31+G(d)	0.20	198
Thioindigo	$\pi \to \pi^\star$	170	PBE0/6-311+G(2d,p)	0.03	199
Triazene	$\pi \to \pi^\star$	5	PBE0/6-311+G(2d,p)	0.11	200
Triphenylamine (DSSC)	Charge-transfer	21	BHandHLYP/6-311+G(2d,2p)	0.28	201
Triphenylcarbocationic	$\pi \to \pi^\star$/Cyanine	45	PBE0/6-311G(d,p)	0.27	202

^{a}Spin-flip TDA calculations; ^{b}Combining the data in these six publications; ^{c}Part of a large set of NIR dyes

spectrum.[250] Secondly, the existence of dimers or larger clusters in solution was examined and it was found that these structures are too weakly bonded to significantly impact the measured spectra.[248] Eventually, the computation of Franck-Condon factors at the ωB97X-D/6-31++G(d,p) level,[251] allowed the perfect reproduction of the measurement (see Figure 2), confirming the vibronic origin of the band shape.[248] Note that the use of a range-separated hybrid or a functional including a large share of exact exchange may be useful to avoid qualitatively incorrect description of the ES PES.[111,112,252–254] As can be seen in Figure 2, only a few individual vibrational modes significantly contribute to the topology of the observed spectra. The first band can be attributed to the bending of the amino groups and the breathing of the aromatic ring bearing the two amines whereas the most intense maximum is related to stretching in the same ring and vibrations of the hydrogen atoms of the amines. This refines the original assumption of strong couplings with the C-N vibrational modes.[247] In a subsequent investigation, we have shown that these vibronic effects have a significant impact on the perceived colour for other amino-substituted anthraquinones.[249] This was made possible by transforming the computed absorption spectra into colourimetric coordinates.[255,256] Indeed, a vertical calculation would predict a yellow hue for Solvent Blue 35 (SB35, 1,4-NHBu-9,10-anthraquinone), whereas it obviously appears blue experimentally. This is just one clean-cut illustration of the usefulness of the calculations of the ES Hessian that pave the way towards more complete (and often more accurate) spectral analysis.
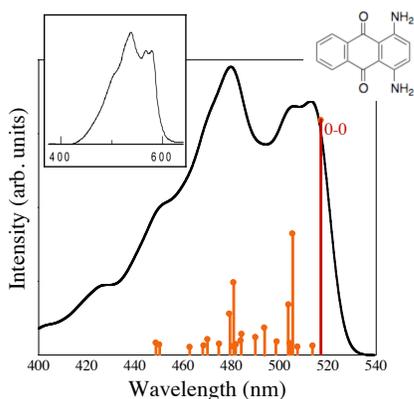
Fig. 2 Comparisons between simulated (both stick and convoluted) and measured (top left panel) visible absorption spectra of 1,4-NH$_2$-9,10-anthraquinone. Adapted with permissions from D. Jacquemin, E. Brémond, A. Planchat, I. Ciofini and C. Adamo, J. Chem. Theory Comput. 2011, **7**, 1882–1892. Copyright 2011, American Chemical Society. The top left panel is adapted with permission from M. S. Khan and Z. H. Khan, Spectrochim. Acta, Part A 2003, **59**, 1409–1426. Copyright 2003, Elsevier.

3.2 $n \to \pi^\star$ chromogens

Most coloured molecules possess at least one strongly dipole-allowed low-lying ES, typically a valence $\pi \to \pi^\star$ or a metal-to-ligand charge-transfer ES for organic and inorganic molecules, respectively. However, there also exist $n \to \pi^\star$ chromogens, where the perceived colour find its origin in a nearly dipole-forbidden ES. Of course, these ES can only play a significant role in the visible absorption when they are well separated from other ES on the energy scale. Three organic chromophores are known to present such feature: N=N (diazo), N=O (nitroso) and C=S (thiocarbonyl).[123] It has been shown that TD-DFT reasonably reproduces $n \to \pi^\star$ transition energies, even in the vertical approximation, irrespective of the applied exchange-correlation functional, provided an hybrid is selected.[257] PBE0 results are shown in Figure 3 for several series of dyes and show a very satisfying correlation between measurements and TD-DFT predictions. Indeed, adding together the data set of Refs 152, 258, 177 and 197, one obtains a set of 169 $n \to \pi^\star$ transitions, characterised by a MAE of 19 nm (0.12 eV). For this panel, a simple linear regression leads a R^2 of 0.96, a correlation slope very close to 1 (0.985) and an intercept very close to 0 (-1.7 nm).
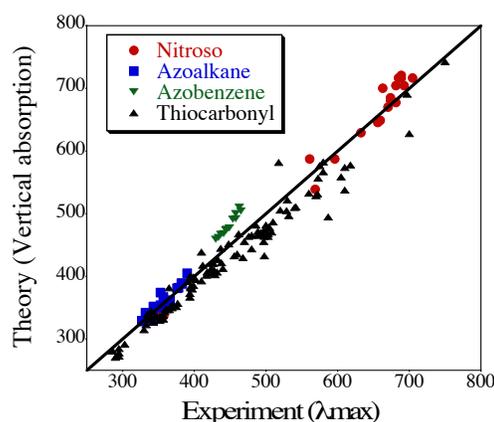
Fig. 3 Comparisons between experimental λ_{max} and vertical absorption wavelengths computed with PBE0. Original data used various basis sets.[152,177,197,258] All data are in nm. The central line indicates a perfect experiment–theory match.

3.3 Cyanines

The prototypical cyanine dyes (streptocyanines) are charged dyes constituted of a chain, containing an odd number of sp^2 carbon atoms, that is capped at its extremities by amino groups. These relatively compact dyes present a sharp absorption band with a shoulder at higher energies, and develop extremely large extinction coefficients.[124] Cyanines re-

main the focus of intense experimental developments, notably in the bioimaging field.[259–261] As stated above, comparisons between TD-DFT $E^{\text{vert–abso}}$ and experimental λ_{max} for cyanines lead very disappointing results, that is large to huge theoretical overestimations of the transition energies are noticed,[134,229,230] despite the apparent simplicity of the problem (indeed, the simple "electron in the box" approach is successful for mimicking the so-called "vinyl shift" of increasingly long cyanines).[262] This methodological difficulty has been related, on the one hand, to the description of the electron correlation difference between the GS and the ES, and, on the other hand, to the fact that the measured λ_{max} significantly deviates from verticality in cyanines.[37,231–236] For the latter aspect, see Section 4.2 for applications accounting for structural and vibrational relaxation effects in cyanine-related compounds.

Despite this limitation, TD-DFT remains a useful tool in the cyanine field as chemical ranking is often preserved.[159,263–272] For instance, Champagne and coworkers have demonstrated that the use of a simple linear correction of the TD-DFT energies allows to calculate experimental λ_{max} with a 10 nm (ca. 0.05 eV) accuracy for nine diverse cyanines, while the presence of the hallmark shoulder could be reproduced as well by applying vibronic corrections.[159] Bertolino *et al.* successfully modelled solvatochromic effects in a series of cyanines using a TD-B3LYP approach,[263] whereas Leszczynski's group found, with a similar protocol, that counterions may play a crucial role by significantly tuning the transition energies in the Cy5 dye.[270] Eilmes performed a similar studies for ketocyanines.[271]

3.4 Charge transfer dyes

As mentioned in the start of this Section, one of the limitation of global hybrids is the modelling of intramolecular charge transfer states. Actually, intramolecular CT transitions that are formed when light absorption induces a "jump" of electronic charge from one part of the dye to another moiety are actively investigated, as they play a key role in light emitting diodes, photosynthesis and solar cells.[273–281] Consequently, the accurate prediction of their spectral properties, that is at hand with range-separated hybrids, mobilised huge TD-DFT efforts, especially during the last few years.[190,226–228,282–296] In the same time, several metrics have been designed to quantify the intensity of CT: i) the Λ diagnostic of Tozer based on the overlap between occupied and virtual orbitals;[222,223] ii) the d_{CT} distance of Le Bahers that measures the separation between the barycentres of density depletion and gain;[297,298] and iii) Guido *et al*'s Δr that relies on the centroids of the orbitals involved in the excitation.[299] Using the second model (see Figure 4), we have shown that in rod like dyes presenting an electron donor (D) and an electron acceptor (A) separated by a π-linker (Π, see Figure 5), the three components should

be simultaneously optimised to maximise the CT, e.g., adding a very strong electroactive group at the extremity of a poor linker is useless.[300]
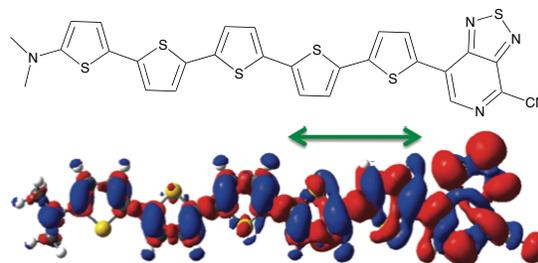
Fig. 4 Density difference plots (blue regions: decrease of electron density, red regions: increase of electron density) between the ES and GS for a typical D-Π-A dye. The green arrow indicates the CT distance, as computed from Le Bahers' method. Adapted with permissions from I. Ciofini, T. Le Bahers, C. Adamo, F. Odobel, D. Jacquemin J. Phys. Chem. C 2012, **116**, 11946–11955. Copyright 2012, American Chemical Society.

Indeed, a particular application of charge transfer dyes is in the field of DSSC. These dyes are composed by a D-Π-A chromophore, the electron acceptor being located close to the surface (see Figure 5). The two moieties can be separated by a linker and the electronic excitation is spatially directed toward the surface. Upon absorption of light, the dye molecules are excited in an ES that is normally higher in energy than the bottom edge of the semiconductor conduction band (CB) so that injection of electrons into this latter is thermodynamically favourable.[139] This first basic requirement for DSSC applications can be found in several CT dyes[301–304] and an *in-silico* screening of the most-suitable dyes could be done by adequately adjusting the energetic levels involved, through *ad hoc* chemical modifications of the chromophore.[305]

However, considering isolated dyes allows only a first screening of molecules used in devices, and a more throughout description is often required, a feat accessible with TD-DFT. Indeed the surface has a direct effect on the dye in polarising its electron density and an indirect one in modifying its 3D structure.[71] Both causes not only modify the dye absorption spectrum but also rule the electron injection efficiency, thus affecting the global yield of the solar cell. Focusing on the electronic properties, the spectral modifications can be due to a simple energy shift of the involved orbitals, as in pyridium dyes,[306] or to a change of the orbital involved in the active electronic transitions.[307] Therefore, these effects can be only analysed (and sometime predicted) by a TD-DFT protocol taking into account the effect of the surface.
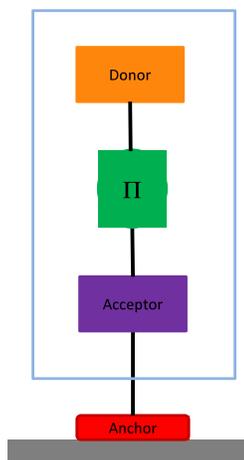
Fig. 5 Sketch of a CT dye adsorbed over a semiconductor surface.

4 Fluorophores

Several key technological applications of dyes are not related to their absorption, but rather to their emission. It is therefore without surprise that a considerable effort has been put in the simulation of the fluorescence of experimentally emitting structures with TD-DFT, that is almost the only reliable theoretical tool available for such studies. Typical goals are to increase the Stokes shift, to redshift the emission and improve its quantum yield (Φ_f, that often decreases with increasing wavelength), to optimise emission for the biological window, or even to create double emitters allowing to produce white OLEDs. We review here several calculations performed on key classes of fluorophores.

4.1 Coumarins and Naphthalimides

Pyranones and naphthalimides can be considered as the two most notable groups of organic fluorescent brighteners,[126] the total world production of these substances exceeding 40 000 tons per year.[129] While pyranones may be divided into two subgroups (coumarins and chromones), three naphthalimides subclasses differing by the relative positions of the three aromatic rings exist: 1,2- 2,3- and 1,8-derivatives. Coumarin, is known since the ninetieth century for its specific flavour and was synthesised for the first time by Perkin in 1882. Besides their interest in pharmaceutical science (anticoagulants), coumarin derivatives are highly fluorescent molecules often absorbing UV photons to emit visible light. In addition, several coumarins exist in cationic and anionic forms, constituting pH-dependent fluorophores.[308–310] 1,8-naphthalimides typically absorb in a 350–450 nm window and emit at significantly longer wavelengths (370–560 nm).[311–314]

Due to their popularity and relatively small sizes,

one can find numerous TD-DFT studies devoted to coumarins,[315] especially in the framework of DSSC applications.[156,226,283,285,316–319] In addition, these dyes are often used by the quantum chemistry community to assess the validity of environmental models,[58,60,282,320–324] as significant solvatochromic effects have been measured, especially in push-pull coumarins. In that framework, Improta, Santoro and Barone have been the first to demonstrate an impressive reproduction of band shapes for the solvated C153 coumarin,[322] a success impossible to reach with gas phase calculations. Besides these rather methodological investigations often limited to a few compounds, there has been other works tackling coumarin's fluorescence with TD-DFT.[325–332] The most statistically significant coumarin set is probably in Ref. 326. With a TD-PBE0 approach, the MAE obtained by comparing $E^{\mathrm{vert-fluo}}$ to experimental λ_{emi} is 0.28 eV for 54 cases, the theory almost systematically undershooting the experimental wavelength. This error is however rather systematic and can be reduced to 0.07 eV by applying a simple linear regression correction.[326] With the rather simple solvation model used in Ref. 326, the Δ^{SS} were found to have ca. 25% error, but this discrepancy can be reduced when more refined solvation approaches are used.[58,323,332] For instance, the ordering of the emission wavelengths of coumarin and its methyl derivatives were better reproduced with a state-specific PCM model than with the standard linear-response approach by Barone and coworkers.[323]

For naphthalimides, and more specifically 1,8-naphthalimides, there are, to the best of our knowledge, less available TD-DFT studies,[175,176,333–338] and only a few of these tackled emission signatures.[176,333,335,336] For the 24 cases treated in Ref. 176, the MAE obtained on the position of the emission band within the vertical approximation, is as small as 0.16 eV, similar to the one reached for absorption (0.13 eV), but such accuracy can only been obtained when solvent effects are accounted for (the gas phase error is 0.25 eV on fluorescence energies). This means that TD-DFT can be used to analyse the emission spectra of molecules with implicit solvation model,[335,336] e.g., in Ref. 335 the authors investigated the relative twisting of nitro and dialkyamino groups in both the ground and the excited states of several derivatives, and related their results to experimental spectral trends.

4.2 BODIPY and related dyes

Among the existing organic chromophores, boron-dipyrromethene (BODIPY) and related fluoroborate structures have been the centre of countless experimental works during the last decade due to their exceptionally sharp and intense emission bands that constitute hallmarks of these constrained cyanines.[339–347] In Figure 6, typical cores of these fluorobo-

rate structures are sketched, and one generally distinguishes them by their atomic sequence, that is, N-B-N, N-B-O and O-B-O fluorophores. In terms of TD-DFT simulations, one can find several TD-DFT $E^{vert-abso}$ computations on these structures [148,348–363] but this of course does not grant access to the emission properties. During the last three years, several works used TD-DFT gradients to model the ES geometrical relaxation and the Stokes shift,[113,364–373] but only a few additionally included ES Hessian calculations, giving access to E^{0-0}.[113,369–373]
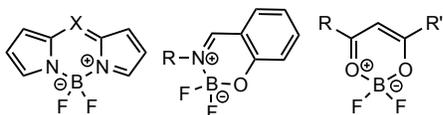
Fig. 6 Representation of typical fluoroborate dyes. From left to right: NBN (BODIPY with X=CH or aza-BODIPY with X=N), NBO and OBO cores.

By cumulating the M06-2X[374] E^{0-0} calculations performed in Refs. 113, 370 and 371 we obtain a set of 102 fluoroborate dyes for which direct comparisons with the experimental absorption-fluorescence crossing point can be performed (see Figure 7).[375] In that Figure, one notices that theory tends to overshoot the transition energies, but the chemical trends are very nicely reproduced, only one clear outlier (a push-pull NBO derivative) being detectable. For the full set, the obtained MAE is 0.17 eV and the corresponding R^2 is 0.96, despite the disparity of the dyes that present both CT and cyanine ES natures. We underline that there are several examples of impressive reproductions of the band shapes of fluoroborate derivatives,[113,370–373] and Figure 8 provides just one striking example of a nearly perfect theory-experiment match.

Given the previous examples, it is crystal clear that TD-DFT can be used for optimising the absorption and emission energies as well as for designing molecules with a redshifted emission. However, an extra important factor is the fluorescence quantum yield. To estimate Φ_f, one should rely, not only on the determined oscillator strengths that provide an incomplete information, but more properly estimate the presence of competitive deexcitation paths. For molecules that do not undergo photochemical processes, the vibrational relaxation can be estimated by computing the Huang-Rhys factors that are a by-product of vibronic calculations.[376,377] Jin and coworkers have performed such kind of investigation for four anilido-pyridine fluoroborates.[369] On top of helping to rationalise the relationship between Δ^{SS} and geometrical constraints, they found that the smaller the Huang-Rhys factors, the larger the fluorescence rates, confirming that non-radiative decay can be estimated from TD-DFT calculations.[369] We obtained also a similar reverse correlation between experimental fluorescence quantum yields and computed Huang-Rhys fac-
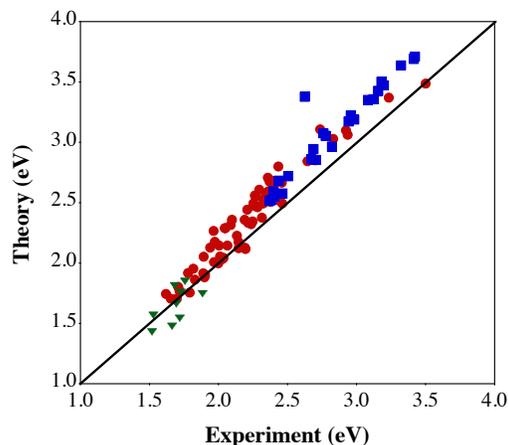
Fig. 7 Comparison between experimental AFCP and theoretical E^{0-0} energies for 9 aza-BODIPY (green triangles),[370] 68 BODIPY (red circles)[113] and 25 NBO (blue squares)[371] derivatives.[375] The central line indicates a perfect theory-experiment match.

tors for meso-substituted BODIPY.[113]
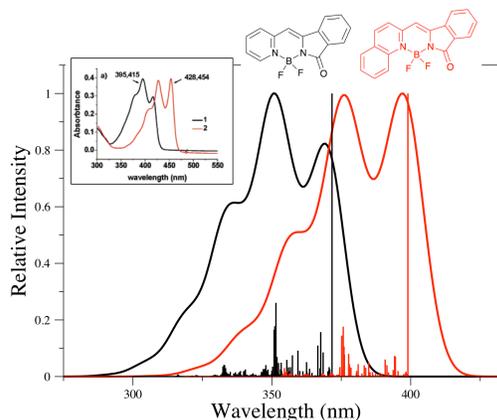
Fig. 8 Comparison between experimental (top left panel) and theoretical absorption spectra for two NBN fluorophores. Adapted with permissions from S. Chibani, B. Le Guennic, A. Charaf-Eddin, A. D. Laurent and D. Jacquemin Chem. Sci. 2013, **4**, 1950–1963. Copyright 2013, Royal Society of Chemistry. The top left panel is reprinted with permission from Y. Zhou, Y. Xiao, D. Li, M. Fu and X. Qian J. Org. Chem. 2008, **73**, 1571–1574. Copyright 2008, American Chemical Society.

4.3 Photoacids and ESIPT

There is a growing interest in fluorescent dyes presenting structural changes in their ES, and the most exploited phenomenon is excited-state intramolecular proton transfer tak-

ing place in molecules presenting (at least) one strong internal hydrogen bond.[378,379] In ESIPT dyes, the most stable isomer differs at the ground and excited states, as a consequence of the increase of the acidity of one proton. The prototypical case is an enol/keto tautomerism displaced to the enol side in the GS, but to the keto side in the ES. Such fluorophores generally present very large Stokes shift and can be used to design ratiometric sensors[380–383] or to build devices presenting dual emission when the ES tautomeric equilibrium is not fully displaced to the keto isomer, allowing emission from the enol.[384]

As this ESIPT reactivity is related to the variation of the acidity between the GS and the ES, the calculation of the pK_a^*, that can be performed with TD-DFT using a Born-Haber cycle,[385,386] can provide a first key information. Indeed experimentally pK_a^* measurements are quite cumbersome. Photoacidity calculations have been performed for several families of dyes including coumarins,[387,388] cyanonaphthols,[389] green fluorescent protein chromophores,[390] quinolines,[391] seminaphthofluorones[392] and stilbenes.[389] It was generally noticed that, on the one hand, the calculations are rather sensitive to the exact details of the selected environmental model, and, on the other hand, an accuracy of 1–3 pK_a^* units can be reached with hybrid exchange-correlation functionals.
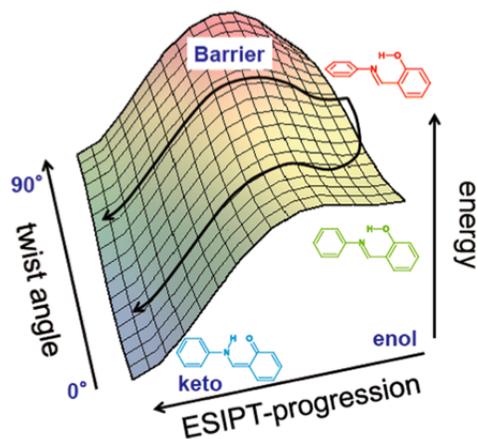
Fig. 9 Qualitative representation of the S_1 PES for *N*-salicylideneaniline inferred from both experiment and TD-DFT simulations. Reprinted with permissions from T. Sekikawa, O. Schalk, G. Wu, A. E. Boguslavskiy and A. Stolow J. Phys. Chem. A 2013, **117**, 2971–2979. Copyright 2013, American Chemical Society.

The modelling of ESIPT can be performed with signle-reference approaches, and several convincing examples of TD-DFT simulations of ESIPT fluorophores can be found in the literature,[329,393–414] but a significant portion of these works deals with model dyes or compact biomolecules. One of the earliest work confirming the validity of TD-DFT for

predicting ESIPT reaction profiles was performed by Aquino and coworkers: they studied five molecules, obtained CC2 or CAS-PT2 reference values, and concluded that TD-DFT (B3LYP) is a valuable approach.[395] Let us briefly present two recent applications. In Ref. 409, the authors investigated salicylideneaniline derivatives and could rationalise the impact of the incoming photon energy on the dynamics of the process. Indeed, with a 370 nm light, only planar structures are excited, and the ESIPT is extremely rapid (50 fs), whereas with a 350 nm incoming beam, mostly twisted molecules were excited and a torsional relaxation has to take place before ESIPT, implying a slower process (see Figure 9).[409] Recently, Houari *et. al.* explored the GS and ES PES of two large (ca. 60 atoms) hydroxyphenylbenzoxazoles dyes, one presenting single keto emission, one displaying dual fluorescence.[384,414] On the energy scale, they found a small ESIPT barrier for both dyes (0.06 and 0.12 eV), but this barrier disappears for the first structure when vibrational corrections are included, indicating a barrier-less transfer for that compound, in perfect match with experiment findings. For the dual-emissive fluorophore, vibronic simulations were performed and allowed to estimate the relative quantum yields of enol and keto emission by comparisons with the experimental shape, that due to overlapping emission bands of the two tautomers could not be straightforwardly analysed by direct experimental means.[384,414]

4.4 Biodyes

The TD-DFT method has also been widely employed to describe absorption and emission spectra of biological systems which are of great interest in medical imaging, biology, neuroscience… In that vein, one often investigates the fluorescent emission at a specific frequency for which there is no significant background from the excitation light, a task possible because relatively few cellular components are naturally (intrinsically or auto) fluorescent. In addition, a protein or another component can be "labeled" with an extrinsic fluorophore, a fluorescent dye that can be a small molecule or a quantum dot. We describe below a few examples in that line of research.

Many area of life science have been revolutionised by the discovery, gene cloning, and expression of the green fluorescent protein (GFP) and other fluorescent proteins that are photostable, present large quantum yield, are non-toxic[415] and are characterised by an emission in the visible domain. Numerous TD-DFT studies have been performed in gas phase and in solution over the two last decades on well-defined FP chromophore models in order to understand and reproduce the spectra[416–422] but studies relying on more complex methods have also been performed to explore the reactivity of their chromophores and the structural changes from one protein to another (see also section 5).[423–428] Clearly one key challenge

is to model how the spectral characteristics of fluorescent proteins are influenced by a structurally fluctuating surrounding. Let us point out two recent QM/MM studies performed with TD-DFT on the FPs. In the first[429], the impact of mutations on the Enhanced Cyan Fluorescent Protein spectra could only be reproduced accurately (ca. 10 nm/0.05 eV deviations) with a model accounting for the complete electronic response of the surrounding (ERS).[66,143,430–432] In that investigation, it was also demonstrated that the geometric deformation, electrostatic component and electronic contribution to the absorption of the chromophore differ significantly for each protein of the series: none can be neglected. In the second recent paper, Amat et Nifosi have investigated chromophore–protein interactions and optical properties using a TD-DFT QM/MM methodology on a very large set of FP derivatives encompassing YFP, Dronpa, mTFP0.7 and the S65T mutant of GFP.[433] Overall, the authors found that CAM-B3LYP excitation energies are considerably blue-shifted (ca. 0.8 eV) with respect to the experimental values. Moreover, the shift within the different FPs is only partially reproduced by TD-DFT. Interestingly, it was found that CASPT2 values are also blue shifted with respect to experimental values and that only SAC-CI reasonably matches the measurements.[433]

Human Serum Albumin (HSA) has been the subject of several QM/MM studies as this protein is abundant in human circulation and is the obligatory way for transporting and storing fatty acids, hormones, metals and, more interestingly, drugs. Using their own QM/MM method[434–437] Assfeld's group modelled the absorption spectra of the tryptophane present in the HSA.[431] Isolated tryptophane presents intense absorption bands at ca. 270 nm and 250 nm. The absorption spectrum of the chromophore extracted from HSA protein is highly similar to the one of solvated tryptophane indicating that no large structural modification is undergone by tryptophane in HSA. The inclusion of electrostatic embedding induces a red-shift with two well-defined and intense maxima at 301 and 345 nm, whereas accounting for "implicit" polarisation using the ERS scheme yields a blue-shifted spectrum (297 and 333 nm).[431] This indicates that the electrostatic contributions due to the surrounding is the prevailing effect (+60 nm) and that the polarisation component is small and has the opposite direction (ca. -12 nm). Aidas *et al.* proposed an investigation of the optical properties of two probes (acridine yellow and proflavin) embedded into different binding site of HSA.[438] They performed a preliminary molecular dynamics simulation to capture the fluctuations of the protein and computed the spectra on the basis of 80 snapshots performed using a polarisable force field for modelling the protein environment. As HSA is characterised by a multitude of binding sites, finding the most favourable site is an issue and Aida *et al.* investigated several sites (denoted BS1, BS2, heme-BS, see Figure 10). The authors found no preferential

site for acridine yellow, but concluded that cationic proflavin probably binds to the BS2 site as this is the only of the three sites leading to a spectral shift in the line of the experiment (ca. -0.2 eV).[438] The same group has made a lot of effort in this direction by communicating relevant paper using TD-DFT QM/MM method on linear and non linear optical properties of N-acetylaladanamide probe in a POPC membrane[439] but also on the importance of accounting for the polarisation effect.[440–442]
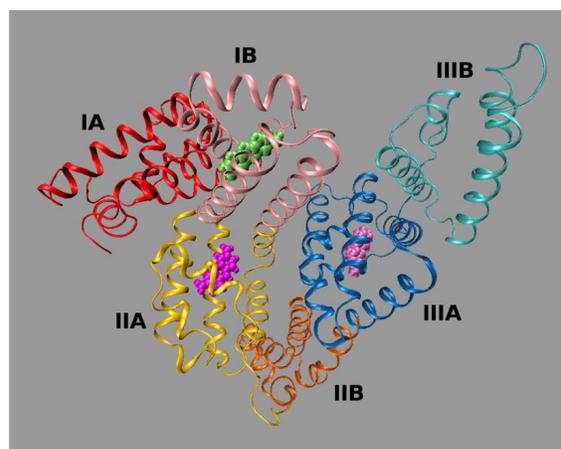
Fig. 10 Domain structure of HSA. Coloured ligands indicate considered binding sites of HSA-BS1 (magenta), BS2 (mauve), and heme-BS (lime). Reprinted with permissions from K. Aidas, J. M. H. Olsen, J. Kongsted and H. Agren J. Phys. Chem. B 2013, **117**, 2069–2080. Copyright 2013, American Chemical Society.

Agren and coworkers used a protocol starting with a Car-Parrinello molecular dynamics followed by TD-DFT QM/MM computations to address the structural and optical properties of the nile red solvatochromic probe in a β-lacto globulin enzyme.[443] The excitation energies of nile red have been computed in the hydrophobic protein cavity, on the surface of the protein as well as in the bulk. Going from the hydrophobic cavity to the bulk, the geometrical changes induce a -33 nm displacement of the absorption maximum while the electrostatic embedding was evaluated to produce a +8/+22/+33 nm shift within the protein cavity/surface/bulk. Within the bulk the authors reported a large effect of the polarisation of the water molecules (+29 nm), but they logically state that this effect becomes smaller in the hydrophobic pocket in which the probe is no more in close contact with its environment. Overall a +93 nm solvatochromic shift has been computed going from the bulk to the protein cavity and this fits the experimental value of +110 nm.[443]

Metalloproteins, e.g., wild-type copper proteins[444–448] and ferritins,[449] have also been the focus of works combining QM/MM and TD-DFT methodologies, and the same holds for chromophores embedded into DNA. For instance,

Mennucci's group has studied the DAPI fluorescent probe (4',6-diamidino-2-phenylindole), a well-recognised marker for DNA, intercalated at two different positions within the doubled stranded DNA (minor grove and binding pocket).[450] Using TD-DFT coupled with PCM and/or MM, they observed that the complexation induced a reduced flexibility of DAPI. For the two sites, the qualitative agreement with experiment is remarkable for both absorption and emission spectra.[450] Mennucci and collaborators compared QM and MM treatments of the DNA pocket. In the minor groove, the differences between both theoretical protocols are triffling whereas for the intercalated situation, the methodological effect is slightly larger, though it still does tune the Stokes shift. In the same line, let us point out the investigations of thiazole orange[451] and polypyridyl ruthenium complex[430,452] intercalated in DNA, that both led to nice reproductions of the experimental trends.

Recently single molecule fluorescence spectroscopy became an attractive tool[453] for studying fundamental aspects of biomolecules interactions at the individual molecules scale but also for exploring excitation energy transfer and quantifying the separation between selected amino acid or nucleic acid residues.[454]. The use of Förster Resonance Energy Transfer (FRET)[455] to determine distances in biomolecular systems relies on the relationship between fluorescence intensity (or lifetime) and inter-dye separation. Indeed, the rate of energy transfer or efficiency of this dipole-dipole interaction is highly dependent on many factors such as the spectral overlap between the emission of the donor and the absorption of the acceptor, the distance between the donor and the acceptor and the relative orientation of transition dipoles (κ), the refractive index of the media , the donor quantum yield and the donor fluorescent lifetime in the excited state in absence of the acceptor. In that framework, many groups have worked on the simulation of FRET with methods like the Transition Density Cube method[456,457] as well as improved approaches.[458–465] There has been much debate on which dipole orientation value (κ^2) should be assigned for particular FRET. If there is no crystal structure available, there is no reliable experimental method to obtain this factor, and an isotropic value is commonly used, considering rapidly rotating dipoles ($\langle \kappa \rangle^2 = 2/3$). However, by doing so, one assumes that the distance between the donor and the acceptor is uncorrelated with the orientation of the probes.[466] Consequently, several theoretical works have been dedicated to the evaluation of κ.[65,467–471] In 2011 Speelman *et al.* established a strategy for generating the donor-acceptor electronic coupling using molecular dynamics trajectories. In this approach, electronic couplings have been calculated within the induced dipole approximation and the transition density cube method using the computed transition dipole moments of the donor and the acceptor as well as their full transition densities. The two transition dipoles moments are next mapped onto the trajectories. Therefore the κ and the

distance between the donor and the acceptor are estimated. For more details, we redirect the interested reader to a recent perspective on the topic.[472]

5 Photoswitches

Of course, TD-DFT has also been used to investigate photochromes, that is molecules presenting two (or more) stable isomers, the conversion from one to the other being triggered by light absorption. Successful photochromes possess large reaction quantum yields, are highly stable and importantly present a strong contrast between the two forms, e.g., one form is coloured/conductive whereas the other is uncoloured/isolating.[473,474] TD-DFT is clearly a method of choice to optimise such contrast, and such task has been performed for the absorption spectra of several series of switches, including diarylethenes,[162–168,475] hemi-indigoids,[476] spiro derivatives[194,477,478] and fulgides[171] (see Table 1). For instance, Nakano and coworkers have used a tuned CAM-B3LYP approach to obtain very accurate estimates of the λ_{max} of dithienylethenes.[162] In 2012, Fihey *et. al.* analysed a panel of diarylethenes substituted by donor and acceptor groups using the B1B95 hybrid functional and evaluated the relationships between several chemically intuitive parameters (bond length alternation, HOMO-LUMO gap, aromaticity, etc.) and the predicted absorption spectra.[475] They found that a large positive Hammet parameter (σ_R) allows to optimise the contrast, that is to obtain large differences of absorption wavelengths between the open and closed isomers.[475] In the same line, Castet, Champagne and coworkers have proposed, in a series of works, to maximise the hyperpolarisability contrast between the two isomers of photochromes (notably spiro derivatives) with the help of theoretical schemes, including DFT and TD-DFT,[479–485] and recently published a complete account on the topic.[486] These authors have particularly focussed on the switches sensitive to the acidity or presence of cations in the environment, e.g., they designed a selective cation spiro-based sensor relying on nonlinear switching,[485] but they have also investigated the impact of the enol/keto isomerism on the first hyperpolarisability response,[484] as well as dihydroazulene/vinylheptafulvene photochromes.[482] A similar investigation of non-linear optical properties of molecular switches has recently been performed by Scuseria's group for fulgides.[487]

In optoelectronic devices, switches are generally attached to noble metal electrodes or nano-particles and should retain their photochromic properties after anchoring on the surface. It has been shown that the preservation of the cyclisation reaction depends on the nature of the spacer linking the molecule to the surface:[488] for diarylethenes linked to a gold nano particle through a phenyl aromatic ring, the photochromic properties are preserved whereas adding a thiophene linker inhibits

the ring-closure reaction. To access the properties of these systems, the strategy developed by Perrier and coworkers consists in modelling the surface by a gold aggregate, Au_n (n = 3, 13, 25) and computing the UV-Vis absorption spectrum using TD-DFT with a range-separated hybrid.This approach was shown to provide reliable information on the loss or preservation of the photochromic properties after immobilisation on a gold surface once the involved molecular orbitals are analysed. [489,490]

For studying the actual photochromic mechanisms, the usual adiabatic approximation of TD-DFT is often unsuited. Indeed, it cannot be viewed as adequate for searching for conical intersections that often play a key role in effective switches. However, several loopholes have been designed to circumvent this limitation of TD-DFT. [23,406,491,492] For instance, Masunov and coworkers have not only studied the ground-state properties of diarylethenes, [493–495] but also used the *a posteriori* Tamm-Dancoff approximation (TDA) of TD-DFT to probe the shape of the potential energy surfaces of the two first excited states for these photochromes. [496] Likewise, Olivucci and Truhlar *et al.* have shown that spin-flip TDA can be used to investigate the isomerisation of conjugated chains. [497]

During the last three years, TD-DFT has also been applied to understand the activity of large multiphotochromic structures, especially those containing coupled diarylethene(s), [49,498–512] that present specific experimental challenges compared to single photochromes, including a larger rate of side reactions leading to photoinactive products and a smaller efficiency of the cyclisation reactions than in the "isolated" monomers. [513–529] Due to the size of these molecules (some have several hundreds of atoms), only qualitative investigations are possible. The generally applied protocol is to use TD-DFT to probe the nature of the excited-states so to determine if a Franck-Condon excitation at a particular wavelength is able to induce an electronic reorganisation triggering photochromism on a given site. We redirect the interested readers to a recent account on the topic. [509]

Several biological systems possess a photoswitchable character such as for derivatives of fluorescent proteins (Dronpa, IrisFP, DsRed, EosFP, AsFP595...), the Photoactivable Yellow Protein (PYP), rhodopsins, etc. Although a wide panel of theoretical studies have been performed on biological photochromes, it is known that conventional TD-DFT is not the most convenient approach, as in many cases, excited states presenting a doubly excited nature play a key role. For this reason, most studies rely on CAS or EOM-CC approaches, [530–538] and the same holds for the rapidly growing field of bioluminescence. [539–541] There are nevertheless, available TD-DFT studies. In 2006, Nemukhin have thoroughly investigated the chromophore of fluorescent protein asFP595 in gas phase and in different solvent for various pro-

tonations state of both the *cis* and *trans* isomers. [542] Vallverdu and coworkers have performed molecular dynamic simulation at two different pH on Cerulean green fluorescent protein (a variant of enhanced cyan fluorescent protein ECFP) in order to tackle open experimental questions. They have rationalised that the the blue shift observed when increasing the pH is due a *trans*-to-*cis* isomerisation. [543] Kongsted's team have found a negligible shift of the lowest-lying bright electronic excitation of the deprotonated p-coumaric acid (pCA$^-$) within the PYP and explained this surprising outcome as the result of a subtle balance between hypsochromic and bathochromic effects. [544] More specifically, it was found that the change in the excitation energy related to the disruption of the planarity of pCA$^-$ inside PYP is nearly canceled by the shift induced by the intermolecular interactions between the chromophore and the protein. [544]

6   Summary

Since the antiquity, dyes have an attractive effect on the human beings, either for their colour or, in the more recent modern age, for their chemistry. The possibility to control their electronic structure, through *ad hoc* modifications of the chemical skeleton, and the associated optical properties, giving colour shades, not only is an example of how chemistry is related to beauty, but also of the crossing point between science and technology. Indeed dye chemistry opens the way to a number of technological and industrial applications, from textile to organic electronics and renewable energies.

In this context, computational chemistry brings its contribution with models and methods able to describe all the subtle phenomena ruling the excited state properties of "real-life" dyes. In particular, Time-Dependent Density Functional Theory emerged in the last decade as one of the most reliable (and easy-to-use) approach allowing the determination of all the energetics quantities involved in light-molecule interactions. These include not only vertical absorption and emission phenomena but also adiabatic energies and 0-0 excitations. If other methods could be sometimes (and for some molecules) more precise, they are not generally applicable, due to unfavourable computer-power scaling or to difficulty in handling all non-electronic effects. This is even true since TD-DFT methods can be easily coupled with models describing complex chemical environments (solvent, molecular cage, surfaces) which tune the electronic properties of the dyes, and are consequently vital when aiming at modelling "real" dye in "real" devices. Finally it should be mentioned that beyond their intrinsic properties, photoswitches and photoacids represent reactive systems, and they thus show how TD-DFT methods could be applied to systems far from energy minima.

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Graphical Abstract
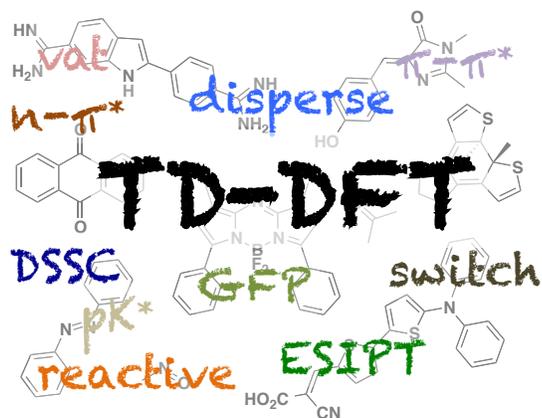
We present a representative panel of TD-DFT applications in the colour chemistry field.

Short bios of the authors

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Denis Jacquemin (born in 1974) obtained his PhD, performed under the supervision of Professor André, at the University of Namur (1998). He next moved to University of Florida for a post-doctoral stay with Professor Öhrn in Quantum Theory Project. He came back to Europe, where he was appointed research associate of the Belgian FNRS (2003) and next Professor at the University of Nantes in France (2010). He obtained an ERC starting grant (2011) and he is a junior member of the Institut Universitaire de France since 2012. His researches are focused on modelling the electronically excited-states in dyes and photochromes.

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Adèle D. Laurent (born in 1985) received her PhD in 2010 under the supervision of Prof. Assfeld at University of Nancy. Next she spent two months at Polytechnic University of Catalonia (Prof. Aleman) before moving to the University of Southern California for a post-doctoral stay (Prof. Krylov). In October 2012 she obtained a permanent CNRS researcher position at University of Nantes. Her work focusses on the modelling of photoprocesses in biomolecules and the developments of hybrid methods.

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Carlo Adamo (born in 1963) obtained his PhD in Theoretical Chemistry at the University "Federico II" of Naples (1995). Between 1993 and 2000 he was Assistant Professor at the University of Basilicata (Italy). In 2000, he moved to ENSCP (France) as Associate Professor where he became Full Professor in Theoretical Chemistry in 2004. In 2011 he was admitted to the Institute Universitaire de France as senior member. His main research interests concern the development of new DFT approaches and their application to various fields of chemistry, including those related to energy production.