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Theoretical investigation of the photochromic properties of [2.2] paracyclophane-bridged imidazole dimers and bis(imidazole) dimers

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[2.2]paracyclophane-bridged imidazole dimers are excellent candidates to build fast photochromic devices with practical applications in full–colour holographic display. Herein, we propose an accurate, yet affordable, computational protocol relying on (TD-)DFT for investigating the structural, thermodynamical and optical properties of these systems, three properties of fundamental importance for their potential applications in fast light modulator devices. Within this theoretical framework, we provide an interpretation of the stepwise two-photon photochromic reaction observed for a symmetric [2.2] paracyclophane-bridged bis(imidazole dimer) and propose a new dissymmetric dimer with potential wavelength-dependent photoactivity.

1. Introduction

Among the plethora of photoactive organic compounds, photochromes have aroused an ever-increasing interest of both experimental[1,2] and theoretical communities[3,4] during the last decades. These compounds exist under two forms, and a reversible transformation between these two isomers, each characterised by specific structural and electronic properties, can take place. Applications of photochromic molecules are very diverse and include drug delivery,[5] or information storage.[6] For thermal (T-type) photochromes, the forward reaction is induced by light whereas the back reaction is controlled by heat. Since in most systems the light-induced colouration spontaneously disappears when the initial colourless isomer is thermally reformed, potential applications ranging from ophthalmic glasses to smart windows can be envisaged for these T-type switches. However, to apply these molecules in optical data processing and real-time holographic materials,[7] it is necessary to reach very high switching rates between these two isomers. Particularly the thermal bleaching rate, that is often a limiting parameter, should be as large as possible. In that vein, Abe and coworkers recently developed photochromic bridged imidazole (Im) dimers showing instantaneous colouration upon exposure to UV light and particularly rapid fading in the dark.[8,9] For instance, this group synthesised a [2.2]paracyclophane ([2.2]PC-) bridged imidazole dimer (**1** in Fig. 1) which presents a photochromic reaction in the μs to hundreds of ms time range, together with a nearly perfect quantum efficiency and an excellent durability.[8,9] Upon photon absorption, this photochromic compound undergoes a homolytic cleavage of the CN bond linking the two perpendicular imidazole rings, leading to the coloured imidazolyl radicals. The UV–Visible absorption spectrum of the coloured isomer is characterised by a broad absorption band extending from ca. 600 nm–800 nm, and this band was attributed to the radical-radical interaction.[10,11] Abe and coworkers have next enhanced the versatility and functionality of this family of photochromes by modifying the imidazole substitution patterns (see **2**–**4** in Fig. 1).[12,13] In contrast to **1** where the 2-position of both Im rings binds to the [2.2]PC moiety, the 4-position of one or both Im rings binds to the PC fragment in **2** and **3** respectively. In **4**, two pyrene moieties are attached to the 2-position of both Im rings with a configuration pattern identical to the one of **3**. The substitution at

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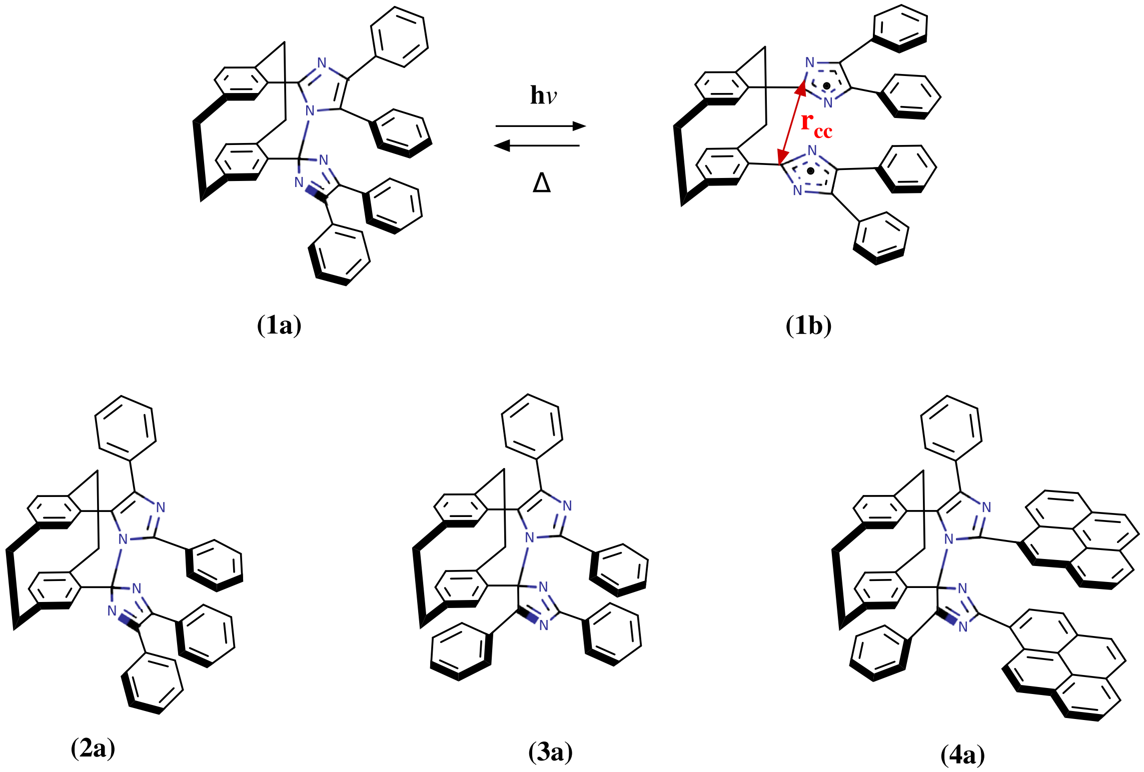
the 2-position of the Im rings was shown to yield drastic changes in both the steady-state and transient absorption spectra, with a red colour observed upon UV irradiation for **4**. These studies have thus paved the way towards real-time RGB full-colour holographic devices as well as to a broader range of applications requiring fast photochromism.

There is now a growing interest in the development of advanced photofunctional materials presenting photophysical properties involving multiple photons and/or molecules.[14–17] In this context, the Abe research group has designed a [2.2]PC-bridged bis(imidazole dimer) (**5** in Fig. 2), a molecule composed of two photochromic units.[18] This compound presents a stepwise two-photon gated photochemical reaction: the absorption of the first photon leads to the formation of a short-lived biradical species (**5b**) which can absorb an additional photon to yield a long-lived quinoid species (**5d**). So far, the number of systems that can undergo efficient stepwise two-photon processes is limited as such process requires that the transient species should be stable and should present a large absorbance. In the past, our groups have used density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations to investigate the photoactivation properties of a large range of multiphotochromic compounds.[4,6,19–21] We have shown that, in these devices, the photochromic properties are often limited since: (i) the spectroscopic signature of the multiphotochromes might turn out to be a simple superposition of those of independent chromophores and; (ii) energy transfers between the photochromic units can inhibit the photochromism of some parts of the multiphotochromes. Theoretical studies thus constitute valuable tools to investigate the interactions between the photochromic moieties and to participate in the design of more efficient optical materials.

In this framework, the first purpose of the present contribution is to set up an accurate, yet affordable, computational scheme for studying the structural, thermodynamical and optical properties of photochromic bridged imidazole dimers. So far, these three properties have been investigated with the help of (TD-)DFT studies at the UmPW1PW91/6-31+G(d,p)//UM05-2X/6-31G(d) level[9,10,12,13] but no extensive benchmark study has appeared. We therefore aim to fill this gap with a methodological study devoted to **1**. We next apply the optimal computational protocol to **2**–**4**. In a further step, we investigate the spectroscopic properties of the multiphotochromic compound **5**, aiming to achieve a deeper understanding of the photochromic reactivity of this complex structure. We finally investigate the photochromism of a new dissymetric [2.2]PC-bridged bis(imidazole dimer), **6** in Fig. 3.

2. Methodology

All the calculations have been performed with the Gaussian 09 package[22] using DFT and TD-DFT calculations to model the ground-state (GS) and the excited-state (ES) properties, respectively. We have tested three different Pople-type atomic basis sets, namely, 6-31G(d), 6-31+G(d) and the more extended 6-311+G(d,p). For the GS geometry optimisations, we have considered two different exchange-correlation (XC) global hybrid (GH) functionals: PBE0[23] that contains 25% of *exact* exchange, E_x^{HF}, and M06-2X[24] ($E_x^{HF} = 54\%$). For the radical species, we have used the broken-symmetry (BS) unrestricted approach and systematically checked the stability of the wavefunction. The localisation of the transition states (TS) has been achieved with the Synchronous Transit-Guided Quasi-Newton (STQN) method and more specifically the QST3[25] approach. For all the optimised structures, vibrational frequencies were computed to ensure that the geometries correspond to either true minima or TS on the potential energy surfaces. In the latter case, we have checked the presence of a single imaginary vibrational mode corresponding to the expected reaction coordinate. For the calculation of the ES properties, we have enlarged the set of tested exchange-correlation functionals and considered three



(1a) (1b)

(2a) (3a) (4a)

Fig. 1. Representation of the different systems under investigation in this work.