

Intermolecular interactions in electroluminescent conjugated materials

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Abstract

We discuss the results of correlated quantum–chemical calculations aimed at addressing the way intermolecular interactions influence the absorption and emission properties of conjugated chains. The nature of the lowest excited states in molecular aggregates is discussed and a special emphasis is given to the effect of chain length and relative positions of the interacting units on the calculated properties. Strategies are suggested that could significantly reduce luminescence quenching in light-emitting devices. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Intermolecular interactions; Molecular aggregates; Light-emitting devices

1. Introduction

Organic conjugated materials emerge as very attractive elements for use in light-emitting displays [1,2]. Numerous studies over the recent years have largely contributed to the design of devices with performances that now compete with their inorganic counterparts. However, there is still a need for fundamental understanding of the solid-state optical properties of luminescent materials, which were shown in many instances to be strongly affected by interchain interactions [3–6]. In this contribution, we investigate the impact of interchain coupling on the absorption and emission properties of conjugated compounds by means of correlated quantum–chemical calculations. We collect here the most relevant results of our recent studies based on a supermolecular approach, in which calculations are performed on clusters of interacting units; we can thus describe the intrachain vs. the charge-transfer character of each excitation in the cluster; this is in contrast to traditional excitonic theories based on perturbative approaches, where the charge-transfer contributions are neglected [7,8]. Our methodology is first to optimize the ground-state geometry of a single chain by means of the semi-empirical Hartree–Fock Austin Model 1 (AM1) method [9] and then to define the relative positions of the interacting units in the aggregate. The optical properties of the whole cluster are subsequently calculated on the basis of the semi-empirical Hartree–Fock intermediate neglect of differential overlap (INDO) Hamiltonian coupled to a single configuration interaction (SCI) scheme, as para-

meterized by Zerner and co-workers [10]; the CI developments involve all the relevant single excitations between π -molecular orbitals.

2. Theoretical methodology

We have initially considered the ideal case of highly symmetric complexes by building co-facial dimers where two conjugated units are exactly superimposed on top of one another [11]. Fig. 1 displays the evolution of the lowest two optical transitions in co-facial dimers formed by two planar stilbene molecules, as the interchain distance goes from 20 down to 3.5 Å; these two optical features result from the interaction between the lowest optically-allowed $1B_u$ excited state of each chain. The theoretical results demonstrate that: (i) the lowest excited state of the dimer is not optically coupled to the ground state, whatever the interchain separation; and (ii) the intensity is concentrated in the second excited state (or in a higher-lying state at short interchain distances, i.e. below 4 Å). This can be qualitatively understood on the basis of a dipole–dipole interaction model [7]: the lowest excited state then originates from a destructive interaction of the two intrachain transition dipole moments, while the second excited state results from their constructive interaction; however, a simple point–dipole approximation provides reliable estimates for the optical splittings only when the interchain separation is larger than the size of the interacting units [11,12]. The calculations establish that the exciton splitting energy increases when the interchain distance is reduced. The splitting is symmetric with respect to the transition energy calcu-

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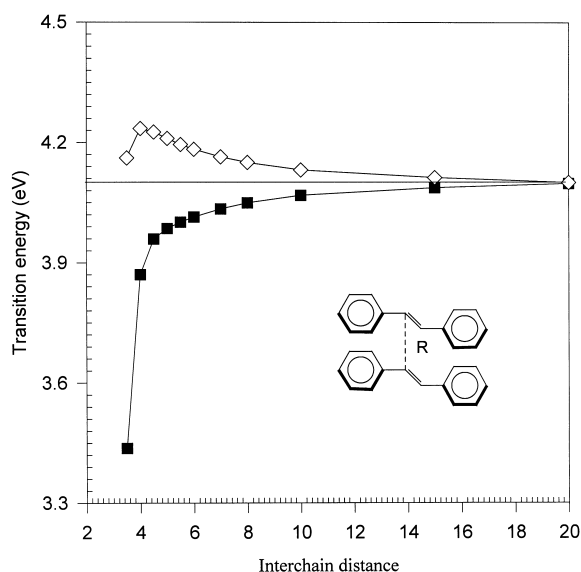


Fig. 1. Evolution of the INDO/SCI-calculated lowest two optical transitions in co-facial dimers constituted by two stilbene molecules as a function of the interchain distance R (in Å). The horizontal line refers to the transition energy calculated for the $1B_u$ excited state of the isolated chain. We stress that the upper value reported at 3.5 Å actually corresponds to the fifth excited state of the dimer, which gives rise to the lowest intense absorption peak.

lated for the isolated stilbene unit for large separations; this does not hold true at the strong interaction limit where charge-transfer contributions become significant.

The calculations thus indicate that interchain interactions in co-facial dimers lead to a blue-shift of the lowest absorption band and a strong attenuation of the light emission from the lowest excited state, due to the absence of optical coupling with the ground state. We emphasize that the same picture prevails when increasing the number of units stacked along the interchain axis and as long as the molecular long axes remain parallel to one another [11]. This rationalizes the dramatic decrease in fluorescence quantum yield of α -sexithienyl (6T) when going from solutions to crystals or thin films where solid-state ordering promotes a parallel alignment of the chain axes [5,6]. Furthermore, it is worth stressing that the Davydov splitting estimated from quantum-chemical calculations performed on clusters of 6T molecules arranged as in their crystalline phase, is in excellent quantitative agreement with the experimental value (on the order of 0.30 eV) obtained from polarized absorption spectra at very low temperature [13].

It is also of interest to investigate the way the optical splitting calculated at fixed interchain distance evolves with the size of the interacting unit. We display in Fig. 2 the evolution of the exciton splitting in co-facial dimers formed by two polyenes separated by 6 Å, as a function of the inverse number of carbon atoms; here, the splittings are calculated with three different formalisms, namely: (i) the supermolecular approach; (ii) the point-dipole approximation; and (iii) an exciton model based on a multicentric

monopole expansion of the electronic transition density, in which the splitting $W = 2|\beta|$ is estimated from the atomic transition densities associated to the lowest optically-allowed transition of a single chain [8]

$$\beta = \sum_{m=1}^N \sum_{p=1}^N \frac{q_1^m q_2^p}{r_{mp}}$$

In the equation, each sum runs over all the sites of a chain and q_1^m (q_2^p) denotes the atomic transition density on site m (p) in molecule 1 (2). Both the supermolecular approach and the exciton model based on atomic transition densities indicate that the exciton splitting passes by a maximum before asymptotically decreasing as the chains elongate [14]. A similar behavior was also reported from INDO/SCI calculations performed on co-facial dimers constituted by oligophenylenevinyls of increasing chain length [11] as well as from a generic study carried out at the Pariser–Parr–Pople (PPP) level within a perturbative approach [15]. In contrast, the point-dipole model yields largely overestimated exciton splittings and an inconsistent chain-length evolution since the splitting increases with N . These results cast strong doubt on any detailed interpretation of optical properties in molecular aggregates based on the point-dipole approximation.

3. Results and discussion

The slight differences between the values calculated within the other two approaches can be attributed to the neglect of the charge-transfer contributions in the excitonic model. Analysis of the chain-length evolution of the optical splittings reveals that the position of the maximum is shifted to longer chain lengths when the interchain separation is increased; the occurrence of such a peak behavior results

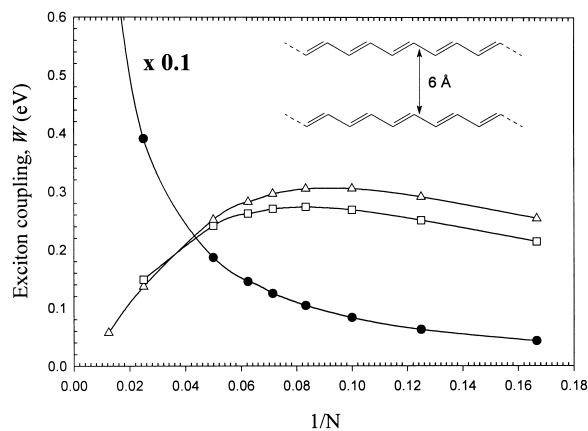


Fig. 2. Evolution of the exciton coupling energy in co-facial dimers formed by two polyene chains separated by 6 Å as a function of the inverse number of carbon atoms N , as estimated from: the supermolecular approach (\square); the point-dipole approximation (\bullet); and the exciton model based on atomic transition densities (Δ). The values obtained within the point-dipole model have been scaled by a factor of 0.1.

from a subtle interplay between finite-size and delocalization effects [14]. The calculations thus suggest that luminescence quenching due to interchain effects is expected to get significantly reduced in well-ordered fully-conjugated long chains; this appears consistent with experimental data showing that concentration quenching, typically observed in dyes, can be absent in conjugated polymers [16].

We now turn to strategies that could be followed to induce significant optical coupling between the ground state and the lowest excited state (emitting) state in molecular aggregates. Two possibilities suggested by the results of previous calculations are: (i) to use highly delocalized conjugated backbones; or (ii) chains that are well separated, for instance due to the presence of bulky substituents or through encapsulation (such as in a dendritic box) [17]. It is interesting to note that, in co-facial dimers, a weak optical coupling is calculated to occur when taking explicit account of the lattice relaxation effects in the lowest excited state (these indeed lead to a breaking in the symmetry constraints since the geometry distortions are mostly localized on a single unit; this points to the mostly intrachain character of the exciton in the lowest excited state) [11]. This result explains the significant increase in radiative lifetime observed in many instances upon interchain interaction [3].

Another approach towards supramolecular architectures with high luminescence quantum yield is to modulate the relative positions of the interacting chains. We have investigated the changes occurring in the properties of co-facial stilbene dimers when performing basic operations such as translations and rotations. The INDO/SCI results show that the most successful approach is to promote a finite angle between the long chain axes of the interacting units [11]. As the amplitude of the angle is increased, the transfer of intensity towards the lowest excited state is amplified and leads to the appearance of a weak absorption feature red-shifted with respect to the lowest absorption band of the single stilbene unit. The impact of interchain interactions is minimized for a perpendicular orientation of the long chain axes, as encountered in spiro-conjugated molecules; this is consistent with recent experimental data revealing the absence of concentration quenching for spiro-type molecules, making them very attractive materials for use in light-emitting devices [18]. Thus, misalignments of chain axes in thin films are not at all detrimental for the solid-state luminescence quantum yield; this has also been recognized in recent studies showing that the efficiency of light emission in poly(*para*phenylenevinylene) (PPV) chains can be enhanced in the solid state through incorporation of *cis*-linkages along the conjugated backbones, which disrupt the chain packing and lead to the formation of amorphous films [19,20].

A different approach, more readily applicable to molecular materials than to conjugated polymers, is to translate chains along their main axis in such a way as to reach a brickwall-like architecture, such as that observed with cyanine molecules in J-type aggregates [21]. The influence

of such an architecture on the luminescence properties can be depicted by considering a three-unit cluster; the initial geometry is defined as follows: to a co-facial dimer (H-aggregate) formed by two stilbene units separated by 4 Å, we add a third stilbene unit aligned along the main chain axis of the lower unit (with an interchain separation of 4 Å between the external carbon atoms). We then analyze by means of INDO/SCI calculations the changes in the optical properties of the cluster as a function of the translational shift of the upper unit of the dimer, as sketched on top of Fig. 3. For the sake of clarity, we provide below a qualitative picture based on the point-dipole approximation, which can be considered here to be qualitatively valid.

In the starting geometry, the lowest two excited states can be assigned to the destructive and constructive interactions of the transition dipole moments of the two units in the co-facial dimer, while the third excited state closely resembles the lowest optical transition of the isolated stilbene molecule. When the upper unit is progressively translated and the three units start interacting efficiently, the whole intensity becomes concentrated in the second excited state, while the

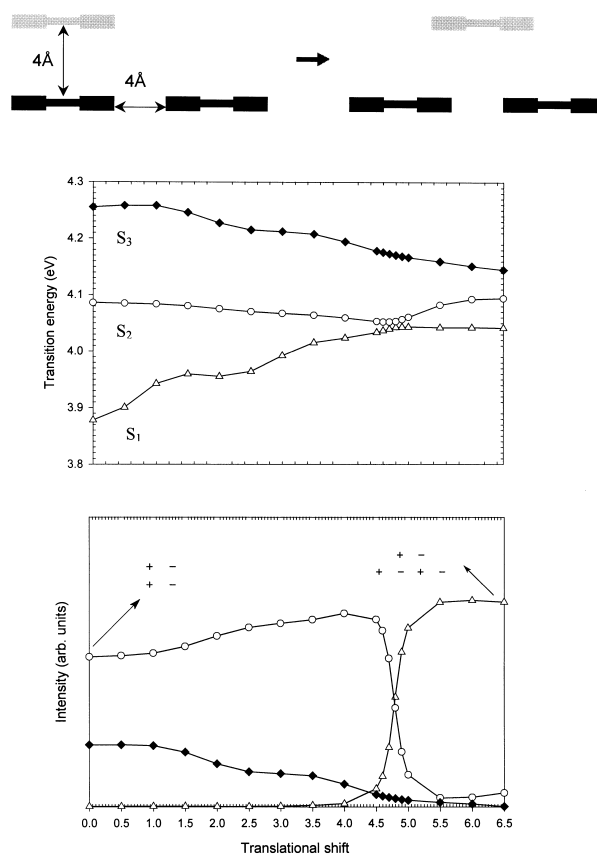


Fig. 3. Evolution of the transition energies (top) and intensities (bottom) of the lowest three excited states (S_1, Δ ; S_2, \circ ; S_3, \blacklozenge) of a cluster formed by three stilbene units, whose initial geometry is sketched in the upper-left corner, as a function of the amplitude of the translational shift applied to the upper unit. We also depict at the two limits of the translational course the nature of the dipole-dipole interactions giving rise to the most intense absorption band.

lowest state remains optically uncoupled to the ground state. However, a sharp crossover in the intensities of the lowest two excited states takes place for a translational shift on the order of 4.7 Å, which corresponds to half the length of the stilbene unit. Before reaching the second crossover in the course of the translation expected for symmetry reasons, we thus find a spatial window having a width of 3.6 Å, where the whole intensity of the cluster is concentrated in the emitting state, and hence, where H-aggregates are converted into J-aggregates. This behavior can be understood within the point-dipole model by the fact that the fully constructive interaction of the three intrachain transition dipole moments there corresponds to the most stable excited state, in contrast to the initial situation (Fig. 3).

4. Conclusion

In conclusion, we have illustrated that correlated quantum–chemical calculations performed on molecular aggregates can prove very helpful to rationalize the influence of interchain effects on the luminescence properties and to design strategies towards efficient light-emitting devices. The supermolecular approach can also give access to a detailed analysis of the one-electron structure of the clusters; this in turn can be used to gain a good theoretical insight into transport properties in crystalline materials on the basis of the calculated interchain transfer integrals [22].

Acknowledgements

The authors acknowledge stimulating discussions with Ph. Millié, R. Silbey, and C. Taliani. The work in Mons is partly supported by the Belgian Federal Government (Pôle d'Attraction Interuniversitaire en Chimie Supramoléculaire et Catalyse (PAI 4/11)), FNRS/FRFC, and the European Commission TMR program (project number 1354 SELOA) and BRITE/EURAM program (Contract BRPR-

CT97-0469 OSCA). JC and DB are research fellows of the Belgian National Fund for Scientific Research (FNRS).

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