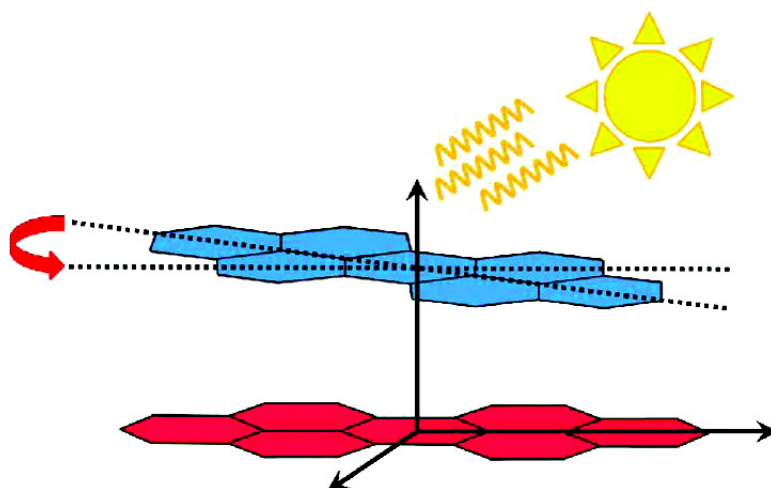Communication

Exciton Trapping in #-Conjugated Materials: A Quantum-Chemistry-Based Protocol Applied to Perylene Bisimide Dye Aggregates

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Exciton Trapping in π-Conjugated Materials: A Quantum-Chemistry-Based Protocol Applied to Perylene Bisimide Dye Aggregates

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Charge and energy transport by π-conjugated molecules are intensively investigated in biological as well as in materials science.[1] Such properties are strongly influenced by intermolecular interactions and the mutual orientation of the single molecules.[2] Self-assembling materials are of special interest since their aggregate structures, and with this their properties, can be steered in a wide range.[3] For a rational design of supramolecular functionalities, detailed knowledge of the effects determining the self-assembly process and the optical properties is required. Absorption and emission spectra provide significant insight, but due to the interplay of various effects their interpretation needs appropriate computational methods.[4] Given the typically large size of the chromophores, the important role of dispersion interactions, and the need to describe electronically excited states, such calculations are very demanding and often limited in accuracy. Nevertheless, various theoretical investigations provide valuable information by assigning absorption spectra.[5] Similar works on emission spectra delivering complementary information about the excited states are rare, however.[6]

In this work we present a new quantum-chemistry based protocol,[7] which provides a quantitative description of both absorption and emission spectra. Applied to perylene bisimide (PBI) aggregates,[8] it provides excellent agreement between theory and experiment and points to a self-trapping of excitons that causes severe limitations for applications of this important class of dyes in organic light emitting devices and organic solar cells. The model also explains results obtained from femtosecond time-resolved spectroscopy[9] and the strong variations in the X-ray structures of differently substituted PBIs.[10]

The measured absorption spectra of the PBI aggregates in methylcyclohexane are shown in Figure 1 (upper left-hand side).[8] The spectrum shows a main maximum around 2.5 eV, with a shoulder at about 2.3 eV. The spectrum was successfully interpreted[11] assuming a dimer structure, dipole–dipole coupling in the excited states, and a single effective vibrational mode for each monomer, while intermolecular degrees of freedom were frozen. The emission spectrum of aggregated PBI (Figure 1, lower left-hand side)[11] possesses a broad, considerably red-shifted band ranging from 1.5 to 2.1 eV. Two additional maxima appear at about 2.2 and 2.4 eV. Attempts to interpret the emission spectrum by the aforementioned model failed, indicating that the assumption of a frozen intermolecular geometry is too simple.

The new protocol[7] employs potential energy surfaces (PESs) for ground and excited states of PBI dimers obtained by appropriate quantum-chemical approaches. The PBI dimer PESs were computed as a function of the distance between the monomer planes, R, of the torsional angle, ϕ, and the longitudinal (X) and transversal (Y)
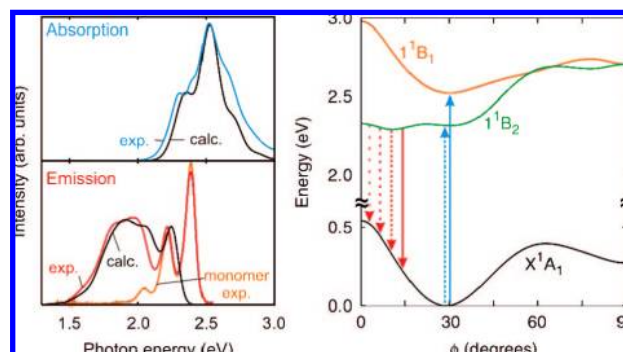

Figure 1. Left: Experimental UV/vis absorption and emission spectra for a mixture of PBI monomers and aggregates in methylcyclohexane (taken from ref 11a) and calculated spectra for monomers and aggregates. Right: Computed PES of ground and excited states.[7]
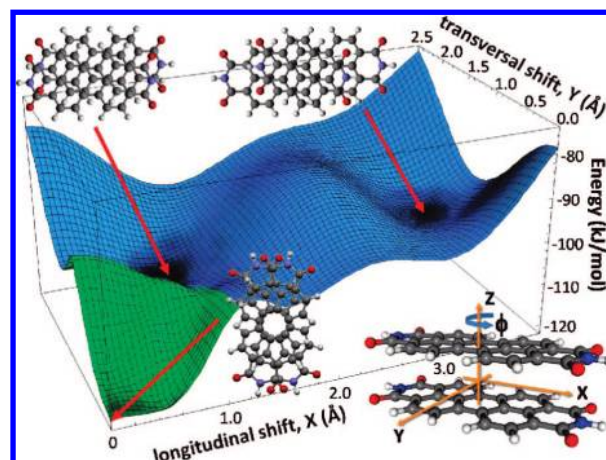

Figure 2. Computed potential energy surface of the ground state (X^1A_1).[7] The rotational angle ϕ is indicated on the right-hand side.

shifts of one monomer as indicated in Figure 2.[7] The ground-state PES was calculated with the DFT-D approach which accounts for dispersion effects by adding empirical corrections to the standard density functional energy.[7,12]

The ground-state PES for $R = 3.31$ Å is shown in Figure 2. The blue surface corresponds to longitudinal and transversal shifts for $\phi = 0°$. The green area depicts the vicinity of the global minimum. In this part ϕ varies from 10° (blue-green border) to 30° (point of origin).[7] Figure 2 reveals that the ground-state PES possesses several local minima within 20 kJ mol^{-1} above the global minimum. This topology nicely explains the relative orientations of differently substituted PBIs in crystals.[10] The global minimum of the dimer is predicted at $R = 3.36$ Å, $\phi = 29.4°$, and $X = Y = 0$ Å. The

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corresponding binding energy at this minimum is computed to be $E_{bin} = -117$ kJ mol^{-1}. The equilibrium torsional angle of about 30° results from attractive electrostatic interactions between the terminal carbonyl and nitrogen groups. The same interactions make the sandwich structure $X = Y = 0$ Å, $\phi = 0°$ highly unfavorable ($E_{bin} = -67$ kJ/mol).[13] The shape of the PES and the binding energies are in good agreement with benchmark computations (counterpoise-corrected RI-SCS-MP2/QZVPP).[7]

The two lowest-lying excited states (1^1B_2 and 1^1B_1) result from the linear combinations of the lowest locally excited states and thus possess neutral character. Since time-dependent density functional theory (TDDFT) with standard functionals was shown to be unreliable for such cases,[15] the excited states were described by the time-dependent Hartree−Fock (TD-HF[16]) method.[7] As dispersion effects lack in TD-HF, they were approximated by the ground-state results.[7] Figure 1 (right-hand side) shows cuts through the potential energy surfaces of the ground (X^1A_1) and the two lowest lying excited states (1^1B_2 and 1^1B_1) along the rotational angle ϕ (for $R = 3.4$ Å, $X = Y = 0$ Å). This coordinate was found to be most important for the description of absorption and emission spectra. The different shapes of the PES of the excited states for $\phi < 30°$ result from the interactions between the transition dipole moments (independent dipole model[17]). To explain the detailed form of the potential curves, and in particular the crossing at $\phi = 60°$, higher order effects have to be taken into account by regarding the respective transition densities.

To simulate the spectra, the model Hamiltonian of the previous approach[11] was employed, but the torsional motion was additionally incorporated using the computed quantum-chemical potentials.[7] Deficiencies of the TD-HF approach were taken into account by a single scaling factor for both excited-state PESs which was obtained by fitting the computed absorption spectrum to the measured one.[7] Figure 1 shows the simulated and experimental emission spectra which are in excellent agreement with each other.

The simulations provide the following picture. Photoabsorption in this H-type aggregate leads preferentially to the higher 1^1B_1-state while excitation to the 1^1B_2-state has a lower probability. The population of the 1^1B_1-state is rapidly transferred to the $^1B_2$ state via the crossing at $\phi \approx 60°$, which is actually a conical intersection.[7] Vibrational relaxation leads to the minimum at $\phi \approx 0°$, where fluorescence is reduced and even becomes dipole forbidden at $\phi = 0°$. This is reflected in the enhanced fluorescence lifetime of the aggregates as compared to the monomers (33 ns versus 3 ns).[11b] The broad band is attributed to the different shapes of 1^1B_2 and X^1A_1 when ϕ tends to zero. Thus, vibrational relaxation of the excited dimer populates a state whose emission maximum is shifted by about 0.6 eV compared to the absorption maximum and which possesses a significantly retarded fluorescence. Because of these properties the exciton energy transfer rate is expected to be reduced making this state a possible dead end for exciton energy transfer. However, this may be influenced by higher order effects.[18]

After subtraction of the monomer contribution (orange line in Figure 1 with vibronic peaks at 2.4 and 2.2 eV), the measured spectrum in solution shows only a small shoulder at 2.2 eV.[7] Thus, the peak in the calculated spectrum at 2.2 eV is too intense. However, the peak intensity is expected to decrease if more internal degrees of freedom and/or higher order aggregates are taken into account.[7] The rest of the simulated spectrum is considerably less sensitive. The intense peak at 2.4 eV is assigned to remaining monomer species, which is in line with thin-film measurements, where monomers are absent.[11] Please note that both peaks are insignificant for our conclusions about the excimer state.

We have proposed a quantum-chemistry based protocol providing excellent agreement between measured and calculated spectra of PBI aggregates. This success indicates general applicability for the accurate description of excited-state relaxation processes in aggregates of large chromophores. Work to use the new model to explain, for example, spectral changes of other PBI-aggregates[19] is under way. Our assignment of the red-shifted band in the emission spectra of PBI aggregates points to a self-trapping mechanism which may limit the exciton transfer properties in aggregates of this important class of dyes.

Supporting Information Available: Further computational details of the applied computational protocol. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Details of the employed protocol and the underlying methods and further discussions are provided in Supporting Information.

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