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# On the Origin of Radiationless Transitions in Porphycenes

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A model for the radiationless deactivation of porphycenes has been proposed based on the theoretical prediction that the lowest electronic state of one of the *cis* tautomeric forms corresponds to an open-shell nonplanar structure. The radiationless channel is provided by crossing of the potential energy surfaces of the ground and lowest excited states along the hydrogen-transfer coordinate. The model explains the large dependence of fluorescence of several porphycenes on viscosity. It also allows prediction of the emissive properties for differently substituted porphycenes.

Porphycenes,[1] constitutional isomers of porphyrin, are important for both fundamental studies and applications. The former include tautomerism involving two inner hydrogen atoms,[2] which occurs as a coherent double hydrogen tunneling in the regime of the isolated molecule and as a rate process in condensed phases. The applications of porphycenes involve photodynamic therapy[3] and information storage. In all of these areas, understanding of spectroscopic and photophysical characteristics is crucial. The latter, however, have not yet been satisfactorily explained. Whereas the parent porphycene (**1**, Scheme 1) and its β-substituted derivatives are strongly fluorescent at room temperature,[4] this is not the case for porphycenes with eight alkyl groups in β and β' positions. Even weaker emissive properties are revealed by *meso*-tetraalkyl derivatives,[5] of which the fluorescence yields and lifetimes in solutions at 293 K are about 3 orders of magnitude smaller than those in **1**. In this work, we provide a rationale for these differences based on experimental and theoretical studies.

The dependence of the fluorescence characteristics on temperature is shown in Figure 1 for **1** and two *meso* derivatives, 9,10,19,20-tetramethylporphycene (**2**) and 9,10,19,20-tetrapropylporphycene (**3**). Contrary to the behavior of **1**, for which fluorescence quantum yield[4] (0.35–0.38 at 293 K) and lifetime change only slightly with temperature, the emission intensity of **2** and **3** increases dramatically at low temperatures, by about 3 orders of magnitude. The corresponding increase is also observed for lifetimes (Table S1, Supporting Information). Fluorescence decays of **2** and **3** are biexponential, which we attribute to the presence of two tautomeric forms, *trans*- and *cis*-A; they were previously detected and characterized for **2** and **3** isolated in supersonic jets.[6] In room-temperature solutions, the S$_1$ state decays in less than 100 ps, whereas at low temperature, nanosecond lifetimes are observed. Transient absorption (TA) spectra show that the radiationless deactivation

SCHEME 1
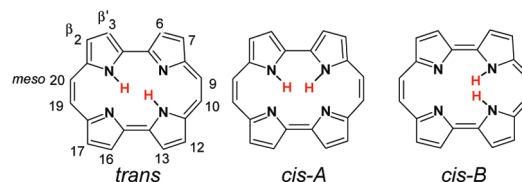
of S$_1$ occurs directly to the ground state; the same decay parameters are extracted from the region of S$_1$–S$_n$ absorption and from the ground-state recovery (Figure 1). No longer-time bleaching is observed, implying that the triplet state is not populated. The activation energy of 2.6 ± 0.3 kcal/mol was obtained for **3** from variable-temperature TA measurements. The results obtained for **2** and **3** agree quantitatively with those reported earlier for **3** from laser photolysis and pulse radiolysis.[5]

The activation energies increase only slightly for derivatives of **2** and **3**, in which the inner protons are replaced by deuterons. On the other hand, we observed that fluorescence yields of *meso*-substituted derivatives are crucially dependent on viscosity. Embedding the chromophore in a polymer film leads to the same effect as freezing the solvent. Nanosecond S$_1$ decays are obtained at 293 K for **2** and **3** in polymers, and lowering of temperature to 15 K leads only to about a 2-fold lifetime increase (Table S1, Supporting Information).

Large viscosity-dependent changes in the emission intensity, although not as drastic as those in **2** and **3**, are also observed for octaalkyl derivatives of **1**, substituted in the β and β'' positions. Fluorescence decay and bleaching recovery in these compounds occur in liquid solvents at 293 K in 100–500 ps (Figure S1, Supporting Information), but these lifetimes increase to nanoseconds for polymer matrixes. A strong indication that the fast nonradiative decay channel involves internal protons is the observation that for the octaethyl zinc derivative, only fluorescence and intersystem crossing are important, whereas in the free base, the sum of their quantum yields is very low.[7]

The huge dependence of the fluorescence quantum yield and decay kinetics on viscosity suggests that the activation of the radiationless decay channel involves large-amplitude distortion

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Letters

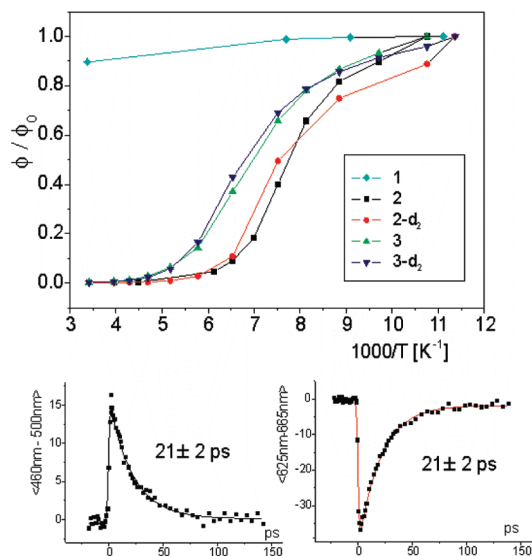*J. Phys. Chem. A, Vol. 113, No. 27, 2009* **7715**

Figure 1. (Top) Comparison of fluorescence quantum yields relative to those at low temperatures (1:1 methanol/ethanol). (Bottom) Kinetic curves for **3** in acetonitrile at 293 K; transient $S_1 - S_n$ absorption (left, integrated in the range of 460−500 nm) and ground-state bleaching (right, integrated between 625 and 665 nm).
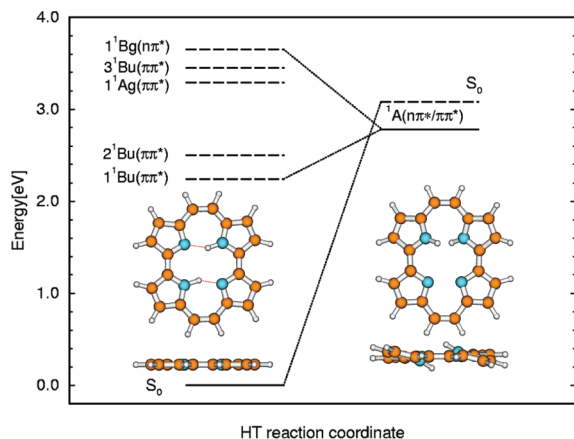

Figure 2. Correlation diagram for electronic-state energies along the *trans−cis*-B hydrogen-transfer reaction coordinate.

of the molecular skeleton. In turn, a lack of viscosity effects in **1** and β-substituted derivatives indicates that in these molecules, the distorted structure lies too high to be thermally accessible. Our goal was, therefore, to find an entrance channel for radiationless deactivation whose position with respect to the S_1 energy would rise in the order tetraalkyl *meso*-derivatives, octaalkyl β,β'-derivatives, unsubstituted porphycene. The model should also be able to account for the viscosity dependence of the emissive properties. Initial searches for conical intersection in *trans*- and *cis*-A tautomers were not successful. However, the CC2 geometry optimization of the lowest excited state of the *cis*-B form, which was known to lie much higher in energy than the *trans*- and *cis*-A species, yielded a negative excitation energy with respect to the closed-shell reference (Figure 2). The resulting geometry of the open-shell *cis*-B form was found to be distorted from planarity. Most important, the energy of this form was calculated to lie slightly above the lowest excited singlet state of the *trans* tautomer, the energy separation being smallest for *meso*-tetramethylporphycene and largest for **1** (see Tables S2−S5, Supporting Information). The lowest electronic state of *cis*-B, 1^1A, involves excitation from orbitals of n and π character into an $\pi*$ orbital (Tables S2−S5 and Figures S2−S5,

Supporting Information); it can be correlated with $1^1B_u(\pi\pi*)$ and $1^1B_g(n\pi*)$ levels of the *trans* tautomer (Figure 2). Thus, we propose that the reason for efficient radiationless deactivation in porphycenes is the crossing between the potential energy surface of the S_1 state of the initially excited species with that of the ground state along the hydrogen-transfer *trans−cis*-B reaction coordinate. This coordinate, apart from hydrogen transfer, mainly involves distortion from planarity by twisting of the two pyrrole moieties in the opposite directions. CASSCF study of **1** indicates a conical intersection at a geometry close to that of the 1^1A state of *cis*-B but somewhat more planar (Figure 6S, Supporting Information). The degree of distortion is much larger in tetra- and octa-substituted derivatives than that in **1** (Figures S6−S9, Supporting Information). It is quite small in 9,20-dimethylporphycene, which fluoresces strongly, although the yield is somewhat lower than that in **1**. These results nicely agree with the prediction that the $1^1A-1^1B_u(\pi\pi*)$ separation is smaller than that in **1** but larger than that in *meso*-tetramethyl and β,β'-octamethylderivatives (Tables S3−S6, Supporting Information).

The two classes of porphycenes for which the deactivation is most efficient and the $1^1A-1^1B_u(\pi\pi*)$ energy spacing is the smallest, 9,10,19,20-tetralkyl and 2,3,6,7,12,13,16,17-octaethyl derivatives, represent two extreme cases of NH···N distances (2.53[1c] and 2.80 Å,[1d] respectively). Though the repulsion of the inner protons in octaalkyl derivatives should be smaller, the distortion from planarity is facilitated by steric interactions in positions 3,6 and 13,16. These results thus confirm the multidimensional character of *trans−cis*-B hydrogen transfer, involving both hydrogen movement and large-amplitude distortions from planarity.

In summary, we postulate a model for radiationless deactivation of porphycenes which is compatible with experimental and computational results obtained for the parent molecule and its doubly, quadruply, and octaalkyl-substituted derivatives. The model can explain the huge viscosity dependence of the radiative properties since in rigid media, the barrier for the molecular twisting should significantly increase. We note, in this context, that radiationless transitions can be very efficient even for ultracold molecules, provided that they are isolated; this has been observed for **2** and **3** in supersonic jets.[6] On the other hand, radiative properties can be recovered even at elevated temperatures by placing the chromophore in a rigid environment. We believe this finding may be important, for example, while designing procedures for photodynamic therapy involving porphycenes.

Supporting Information Available: Materials and methods, computational details, fluorescence quantum yields and lifetime values, molecular orbitals, and calculated energy levels. This material is available free of charge via the Internet at http://pubs.acs.org.

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