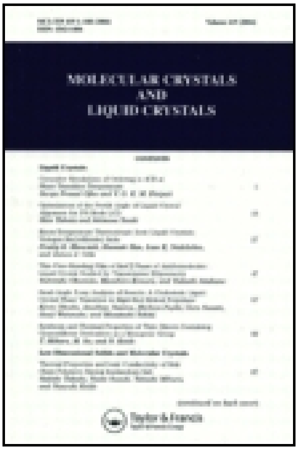

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Photoswitching Intramolecular Energy and Charge Transfer

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Light controlled on- and off-switching of intramolecular energy and charge transfer is demonstrated in donor-switch-acceptor (D-S-A) supermolecules. The supermolecules are designed based on our experience on donor-bridge-acceptor (D-B-A) systems. Switching function is achieved by incorporating optically bistable photochromic fulgides and diarylethenes and proved via fs transient absorption. For both transfer processes, the transfer function is suppressed in the closed form of the switching sub-unit.

Keywords: photoswitch; charge transfer; photochromism

INTRODUCTION

Donor-bridge-acceptor model systems for photoinduced intramolecular energy (ET) and charge transfer (CT) processes have been investigated in our group extensively searching for structural control of transfer functions and dynamics. Appropriate combinations of these bridging sub-units as well as their substitution positions are found which are different for the occurrence and efficiency of energy and charge transfer, respectively [1–4]. To extend functional-

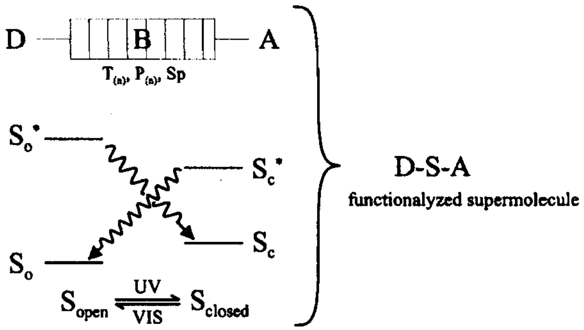

FIGURE 1: Functionalized supermolecule D-S-A combining suitable energy/charge transfer systems with optically bistable switch S, schematic.

ity in multi-component molecular D-B-A systems additional optically bistable sub-units have been integrated allowing for light controlled on- and off-switching of intramolecular transfer (fig. 1). Photochromic molecules (fulgides, dithienylethenes) which are photoconvertible between thermally stable open- and closed-ring isomers [5–7] and switchable at ultrafast time-scales [8–10] are particularly well suited.

PHOTOSWITCHABLE TRANSFER SYSTEMS

The energy transfer system **1** (fig. 2, above) is based on a thienylfulgide derivative substituted with anthracene as donor and coumarin as acceptor. The photochromic performance of the fulgide is retained allowing for λ-selective activation of the switch [11]. Reversibel switching of energy transfer in **1** is evidenced already in steady-state experiments by monitoring the intensity of the acceptor fluorescence during photoconversion process. In the open-ring form **1a** energy transfer and fluorescence intensity are switched "on", in the closed-ring form **1b** switched "off".

In the charge transfer system **2** (fig. 2, below), the donor anthracene is linked to one thiophene sub-unit of the dithienylethene switch via

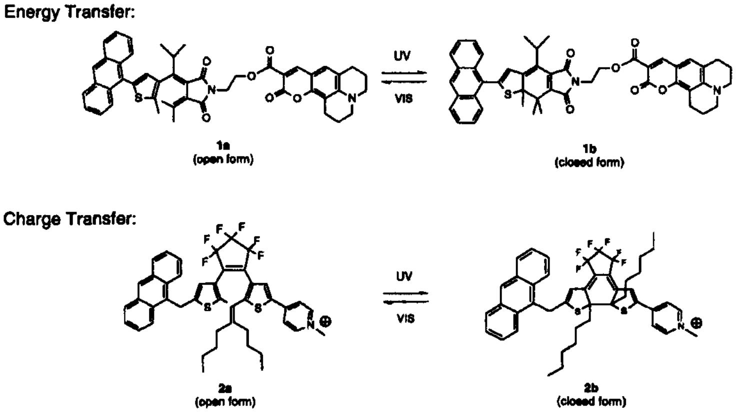

FIGURE 2: Molecular structure, schematic, of open and closed isomers of supermolecules **1** and **2** for switchable ET and CT, respectively.

a methylene-spacer, whereas the pyridinium acceptor is attached in 4-position directly to the other thiophene. This kind of linkage of donor and acceptor is essential for the occurence of charge transfer in thiophene-bridged systems [3].

FS TRANSIENT ABSORPTION

Time-resolved absorption spectra and transients have been measured at 300K for **1a** in polymer (PMMA) and for **2a** in acetonitrile (fig.3, **1a**: left, **2a**: right). In both cases the spectra at short times after fs pulse-excitation at 25830cm^{-1} reflect the excited state absorption of the donor anthracene D^* (absorptive signal with maximum at about 17100 cm^{-1}) which immediately builds up within the instrumental rise time, but decays with measurable time constant of $\tau_{ET}^{decay}(D^*) = 0.85\,ps$ and $\tau_{CT}^{decay}(D^*) = 1.7\,ps$. The spectra of **1a** and **2a** evolve, however, differently towards longer times. For **1a** an emissive signal component (minimum at about 20300 cm^{-1}) is

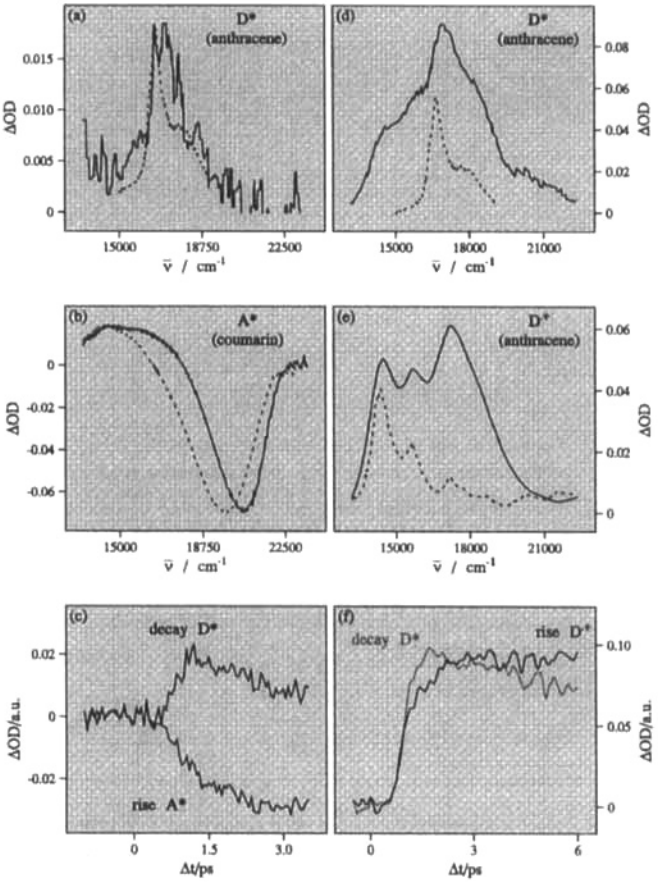

FIGURE 3: Above: Comparison of fast and slow transient absorption signals, D-S-A molecules **1a**: (a) and (b), left; **2a**: (d) and (e), right. (- - -) spectra of anthracene [12], coumarin and anthracene radical cation [13] as reference. Below: Signal rise and decay for **1a** (c) and **2a** (f).

built up in the blue spectral region, in contrast to an absorptive signal in the red for **2a**. The blue signal corresponds to that of the unsubstituted acceptor coumarin (A^*), the red to that of the anthracene radicalcation ($D^{\cdot +}$) exhibiting characteristic vibronic progression (superimposed is the signal of the dithienylethene sub-unit with maxium at 17500cm^{-1} due to partial direct excitation). Remarkably, the rise times of blue and red signal are equal to the corresponding decay times given above, $\tau_{\mathrm{ET}}^{\mathrm{rise}}(A^*) = \tau_{\mathrm{ET}}^{\mathrm{decay}}(D^*)$ and $\tau_{\mathrm{CT}}^{\mathrm{rise}}(D^{\cdot +}) = \tau_{\mathrm{CT}}^{\mathrm{decay}}(D^*)$ (see fig. 3 c and fig. 3 f). The interrelationship of the respective excited state populations is evident. Thus these time constants represent the transfer times of energy $\tau_{\mathrm{ET}} = 0.85$ps and of charge $\tau_{\mathrm{CT}} = 1.7$ps. While switching of energy transfer is already verified by steady-state experiments (see above), switching of charge transfer can only be oberved in transient absorption measurements. In the closed-ring form **2b**, measured under the same experimental conditions, no radicalcation absorption of anthracene is detected.

ENERGY LEVEL SCHEME FOR SWITCHABLE ET-/CT-TRANSFER

The concept of combining intramolecular transfer capability and optical bistability in D-S-A systems (fig. 1) has been demonstrated to be

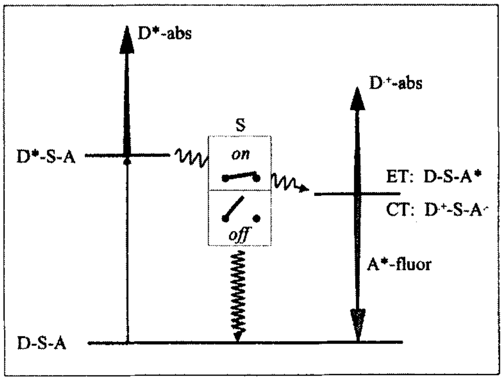

FIGURE 4: Energy level and detection scheme for on-/off-switching of photoinduced intramolecular transfer (ET and CT, respectively).

successfull. It allows for the first time the direct proof of photoswitchable intramolecular transfer (of ET and CT in **1** and **2**, respectively) via transient absorption. A simplified energy level scheme applicable to both cases is derived from the experimental results (fig. 4). In the open-ring form of the supermolecule (switch function "on"), after excitation of the donor (D^*) ultrafast transfer of energy or charge to the acceptor is possible and detected by monitoring the excited state population of acceptor A^* or of charge transfer state $D^{\cdot+}$-S-$A^{\cdot-}$, respectively. Instead, in the closed-ring form (switch function "off") the excitation energy relaxes to the lowest energy level of the supermolecule, given by S, where it is damped radiationless.

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