ULTRAFAST ELECTRONIC ENERGY FLOW IN A BICHROMOPHORIC MOLECULE

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Dedicated to Professor Rudolf Zahradnik on the occasion of his 70th birthday.

The intramolecular electronic excitation energy flow was investigated in a specially designed bichromophoric molecule, 2-(3-benzanthronylamino)-4-(1-pyrenylamino)-6-chloro-1,3,5-triazine (**1**) and was compared with the behaviour of two relevant component model compounds that closely mimic the photophysical properties of acceptor and donor sub-units in the bichromophore. Electronic absorption and fluorescence spectroscopy was applied (including fluorescence anisotropy and decay kinetics measurements with nanosecond to femtosecond time resolution) in order to resolve the energy relaxation process on a real time. An unambiguous piece of evidence is reported for an ultrafast process which leads to practically instantaneous population of the emitting state of the acceptor sub-unit after selective ≈200-fs-excitation of the donor sub-unit. This first direct observation of extremely fast energy transfer in a stiff bichromophore is significant for further development of relevant theory. Two conceptually different approaches to explaining such fast energy flow are discussed.

Key words: Intramolecular electronic energy transfer; Bichromophore; Ultrafast excited states relaxation; Vibronic coupling of electronic states; Time-resolved fluorescence anisotropy; Electronic absorption spectroscopy; Fluorescence spectroscopy.

Advance in understanding of the mutual interactions among chromophores under a situation, when minimally one of them is electronically excited, is crucial both to gaining insight into some elementary processes in nature (*e.g.* primary steps in photosynthesis, dynamics of photochemical reactions, *etc.*)[1], and to designing new molecular materials for technical application (*e.g.* non-linear optical materials for optoelectronics[2]).

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The optical properties of molecular aggregates consisting of more than one interacting chromophores are considered to be non-additive in that properties of the aggregate are often quite distinct from the simple sum of properties of the individual chromophores. It is well known that excitation of an assembly of identical chromophores may usually be described as delocalized over the system, and that the interchromophore interactions lead *e.g.* to excimer fluorescence or spectral line splitting. In molecular assemblies comprising different chromophores, however, the excitation may be localized (at least temporarily), and then be transferred to another chromophore. This process is known as the electronic energy (or excitation) transfer (EET) and was first described by Forster[3] in 1948 as resonance energy transfer due to dipole–dipole interactions (*i.e.* for allowed electronic transitions). For comprehensive description of the Förster theory see refs[4,5].

The first attempt to describe exciton interactions mediating EET in the case of forbidden electronic transitions was made by Dexter[6], who took into account higher order interactions such as dipole–quadrupole and dipole–magnetic dipole, and the exchange effects originating from orbital overlap. His theory in 1953 was originally formulated for solid state, but it is applicable to molecular systems as well. When the chromophores are bound by a chemical (covalent) bond, then the previously neglected "through-bond" interactions may play an important role or may even prevail. In the most simple case it is an interaction through σ-bond orbitals connecting both chromophores (see ref.[7] and references quoted therein). When direct overlap of the interacting chromophore orbitals is not negligible (regardless of whether the chromophores are connected chemically or not), the interaction can be viewed as being mediated by (virtual) charge transfer (CT) states, and it is called a "through-configuration" interaction. The first quantitative discussion comparing triplet–triplet energy and electron transfers was published by Closs[7]. As for singlet–singlet energy transfer, however, there have been few quantitative treatments on a general level (and in relation to electron transfer). A series of papers devoted to such theoretical analyses of exciton interactions responsible for energy transfer (and to their relative importance) was published recently by Paddon-Row and Scholes (ref.[8] and those quoted therein). For comprehensive survey on basic theoretical concepts of radiationless transition dynamics and related phenomena see the quoted monographs[9].

One of the most recent advances in supramolecular photochemistry[10] and photophysics is the targeted synthesis of a binuclear "rod-like" Ru–Os complex exhibiting oriented excitation energy transfer[11]. A nice application of such vectorial transfer was a membrane structure study[12]. Both these studies indicate the need to better understand the exciton interactions involved and the energy transfer mediated by them.

We have recently studied the photophysics of two groups of fluorophores: *N*-substituted 1-aminopyrenes and *N*-substituted 3-aminobenzanthrones. Also, the basic spectroscopic properties of a new bichromophoric compound connecting such two

fluorophores *via* triazinyl spacer were investigated in order to establish a model compound exhibiting intramolecular excitation energy transfer while no (or a minimal) electron transfer takes place. More than 25 model compounds (including some new ones, specifically designed and synthesised for this study) were investigated so far. A rather detailed understanding of both 3-aminobenzanthrones (*i.e.* the bichromophore acceptor-part models)[13–15] and relevant 1-aminopyrenes (*i.e.* the donor-part models) photophysics[15,16] was achieved. Simultaneously, initial spectroscopic studies of the aminopyrene–chlorotriazine–aminobenzanthrone type of bichromophore indicated extremely fast electronic excitation energy transfer within this supramolecule[17]. Nonetheless, the mechanism of the energy flow and the interactions between the fluorophores acting possibly as electronic energy donor and acceptor across the optically non-active spacer responsible for this rapid process still have to be clarified in more detail. In this paper we will present new unambiguous evidence for ultrafast electronic excitation energy flow in the bichromophoric compound occurring on a time-scale of a few hundred femtoseconds; after summarizing its most important spectroscopic and photophysical properties that shed light on the dynamics of energy flow, we will suggest a consistent explanation for this surprisingly efficient transfer process.

EXPERIMENTAL

Syntheses and Materials

The synthesis of **1**, **2** and **3** compounds was described elsewhere[13,16]. Spectral grade dimethyl sulfoxide (DMSO) solvent (Merck Uvasol for steady-state measurements and Wako (99%, Lu) for fluorescence up-conversion experiments) were used without further purification, after a routine spectroscopic check of their quality.

Spectroscopic Measurements

Absorption spectra were measured with a Perkin–Elmer 555 spectrophotometer. Typical concentrations were of the order of 10^{-6}–10^{-5} mol/l (depending on the compound measured), which yielded optical density ≈0.3 at the main absorption maximum in a 1 cm cell. Steady-state fluorescence excitation, emission and anisotropy spectra were measured using a FS 900 photon counting spectrofluorometer from Edinburgh Instruments. The fluorescence quantum yields were determined by integrating the area under the emission spectrum and comparing it with that of quinine sulfate standard solution (q_F = 0.54 in 0.05 M H_2SO_4). The reported data correspond to aerated solutions.

Time-Resolved Spectroscopic Measurements

The fluorescence lifetimes and decay kinetics with sub-ns time resolution were measured using the time-correlated single photon counting (TCSPC) method, either by an Edinburgh Instruments FL900 spectrofluorometer, or by a home-built TCSPC set-up described previously[15,18]. Fluorescence decay kinetics with sub-ps time resolution was acquired by the fluorescence up-conversion method. The method in general is described in the literature[19,20]. We used the following experimental setup: the sample solution (in 0.5 mm optical pathlength flow cell) was excited by frequency doubled output pulses from Ti : sapphire laser (CRAY MXR Inc.) pumped by Spectra Physics Beamlok CW

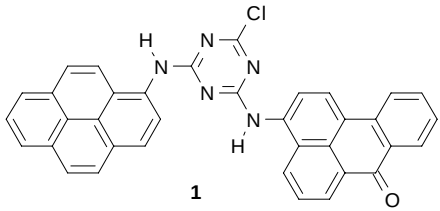
multiline Ar-ion laser; the polarization plane of the exciting radiation was adjusted by a halfwave plate to be either parallel or perpendicular to the polarization plane of the probe beam formed by the fundamental radiation of the Ti : sapphire laser; the emitted fluorescence radiation was focused into a 0.5 mm BBO crystal, together with the probe beam which passed along a variable optical path controlled by an optical delay unit. The intensity of the up-converted light was measured by an R585S (Hamamatsu Photonics) photomultiplier operated in photon counting regime and attached to a monochromator. The time-resolution of the setup was from 150 to 190 fs at different wavelengths, measured as the full width at half maximum of crosscorrelation function. The steric angle for collection of fluorescence was 0.02 steradian.

Sample Preparation

The samples for steady-state fluorescence measurements were prepared by preparative TLC on Silufol UV 254 silica gel. For absorption, and particularly, for fluorescence up-conversion measurements where higher sample concentrations were necessary, several times recrystallized samples were used.

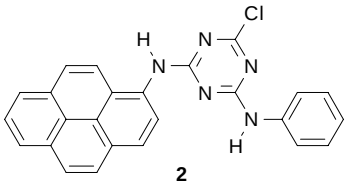
RESULTS AND DISCUSSION

In order to study inter-chromophore interactions in a bichromophoric molecule as **1** (called here BCH), one needs to have a detailed understanding of the behaviour of the isolated chromophores without any mutual interactions. Each of the model compounds, the model donor **2** (called here MD) and the model acceptor **3** (called here MA), was designed and synthesized to mimic most closely the situations experienced by the pyrene-based and benzanthrone-based chromophores in the bichromophore BCH. For the sake of clarity and consistency, we will restrict the presentation and discussion to results obtained in dimethyl sulfoxide solvent.



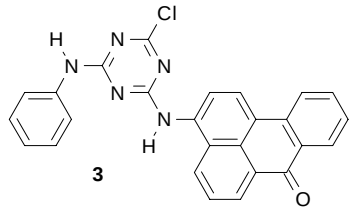
1

2-(3-benzanthronylamino)-4-(1-pyrenylamino)-6-chloro-1,3,5-triazine



2

2-(1-pyrenylamino)-4-(phenylamino)-
-6-chloro-1,3,5-triazine



3

2-(3-benzanthronylamino)-
-4-(phenylamino)-6-chloro-1,3,5-triazine

The previous studies[14,15] proved, that the triazinyl ring used as a spacer, though optically non-active itself, influences the photophysics of the both chromophores attached. Based on comparisons over a whole range of different model compounds, MD and MA described here were chosen as the best possible representatives in terms of spectroscopic, photophysical and photochemical properties suitable for the aims of this study; the MA and MD have the conjugate chromophore replaced by aniline. It is to be stressed that this aniline group, though a chromophore itself, does not influence the spectra of the opposite pyrene-based or benzanthrone-based chromophore within the range of energies relevant for our study of the bichromophore BCH. *N*-(triazinyl)-1-aminopyrene and *N*-(triazinyl)-3-aminobenzanthrone derivatives having a methoxy or chloro substituent instead of aniline also exhibit the same spectra in the 300 to 700 nm region, but the fluorescence kinetics of anilino derivatives is much more similar to that of BCH.

By comparing the steady-state spectra of BCH, MD and MA (see Fig. 1) we clearly see that BCH effectively consists of two chromophores that essentially preserve their identity. In other words, by chemical connection of the original chromophores *via* the triazinyl ring, no new conjugated π-electron system appears. Obviously, the absorption spectrum of BCH can be resolved into two components, each of which resembling the spectrum of either MA or MD. Nevertheless, there is a spectral region where the spectra are non-additive, clearly indicating interactions between the two chromophores in

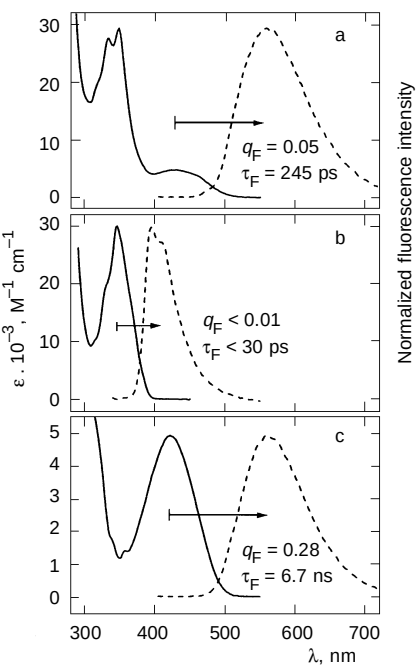


FIG. 1

Steady-state absorption (full line) and fluorescence emission (dashed line) spectra of the bichromophore BCH (a), model donor MD (b), and model acceptor MA (c) compounds in DMSO solvent. Origin and head of each horizontal arrow indicate excitation and emission wavelengths, respectively, used for fluorescence lifetime (τ_F) measurements; during fluorescence quantum yield (q_F) measurements several excitation wavelengths spanning the longest wavelength absorption band were used. Note the difference in *Y* axis scaling on the panel (c)

BCH: BCH absorption around 350 nm is similar to, but not quite a direct, sum of the MD and MA absorptions. It is important to note for further spectroscopic analysis of BCH that its donor (pyrene) part absorption in the visible region above 400 nm is negligible (see MD spectrum), which makes it possible to selectively excite the acceptor (benzanthrone) part of BCH. In a similar way, a preferential (though not exclusive) excitation of the donor (pyrene) part of BCH is possible in the 340–360 nm region, where the absorption of the MA compound is much lower than that of the donor (see MA and MD spectra in Fig. 1, note the different scales for the extinction coefficient ε).

The model acceptor MA fluoresces rather intensively in the yellow-green visible region, in a pattern similar to other triazinyl derivatives of 3-aminobenzanthrone[14]. The model donor MD does fluoresce as well, but with much less intensity and in the blue spectral region. A short fluorescence lifetime and low quantum yield of MD fluorescence in DMSO are typical features of *N*-(triazinyl)-1-aminopyrenes that have chlorine attached to the triazine moiety. The corresponding blue fluorescence is hardly visible in the case of BCH; it has the intensity below that of Raman scattering of DMSO (in solution used for fluorescence measurements). As can be seen by comparing MD, MA and BCH emission spectra in Fig. 1, virtually all detectable BCH emission comes from the benzanthrone (acceptor) chromophore which holds for any excitation, even into the donor-part absorption region.

This conclusion about the origin of the BCH fluorescence emission is further supported by the BCH excitation spectrum: wherever fluorescence is detected within the broad emission band, the excitation spectrum is almost identical to the BCH absorption spectrum (except for the intensity ratio of two main absorption bands).

The important fact that donor absorption in BCH exclusively leads to an acceptor-like emission rises a question about the molecular mechanism responsible for this efficient transfer of excitation energy. There are two conceptually different ways to explain this experimental observation. (i) Excitation into the MD-like absorption band leads to an excited state localized at the donor part of BCH. Consequently, due to excited state donor–ground state acceptor interaction, electronic energy is very rapidly transferred to the acceptor part leading to exclusive emission of acceptor fluorescence. (ii) Some of the electronic excited states of donor and acceptor are somewhat vibronically coupled in such a way that excitation into the MD-like absorption band leads to an excited state that is partially delocalized across both chromophores. Thus, the subsequent electronic and vibrational relaxation can proceed very efficiently *via* acceptor (MA-like) states leading to only acceptor fluorescence emission.

According to the MA fluorescence anisotropy excitation spectrum (see Fig. 2, upper panel), there exists at least one electronic absorption band of MA in the 330 to 360 nm region, which is clearly distinct from the one responsible for the broad absorption around 420 nm. The existence of additional MA excited state(s) is further supported by detailed features of the MA absorption (see the small peak at 360 nm, Fig. 1). Our

previous aminobenzanthrone study[14] allows us to assume that the state in question is the S_3-state having a ππ* character, while the broad absorption 420 nm band corresponds to $S_0 \rightarrow S_1$ (ππ*) transition, and that the transition to S_2 (nπ*) state is forbidden and spectroscopically hidden by the former band. Although the absorption in 330 to 360 nm region (including that *via* the assumed S_3-state) is very weak, it should be noticed that such MA excited states are energetically close to the MD excited state responsible for the main MD absorption peak at 345 nm.

Contrary to the MA fluorescence anisotropy discussed above, the anisotropy of BCH fluorescence (detected at the same wavelength as for MA) is smooth throughout the whole 330 to 385 nm region, and a step-like change takes place in between 375 and 390 nm only. These wavelengths coincide with a saddle point between the two (MA- and MD-like) absorption bands of BCH. The fluorescence anisotropy excitation spectrum of BCH thus qualitatively differs from that of MA in both shape and magnitude of anisotropy, while it is similar to MD spectrum (not depicted) which is smooth throughout the whole 330 to 380 nm region. We can therefore conclude that BCH absorption in this region is mainly governed by donor transitions.

The excitation wavelength dependence of the BCH fluorescence quantum yield, as depicted in Fig. 2 (bottom panel), provides an independent piece of evidence for the presence of two different excitation/relaxation pathways in BCH. The decrease of BCH fluorescence quantum yield under excitation below 390 nm indicates the existence of additional non-radiative losses.

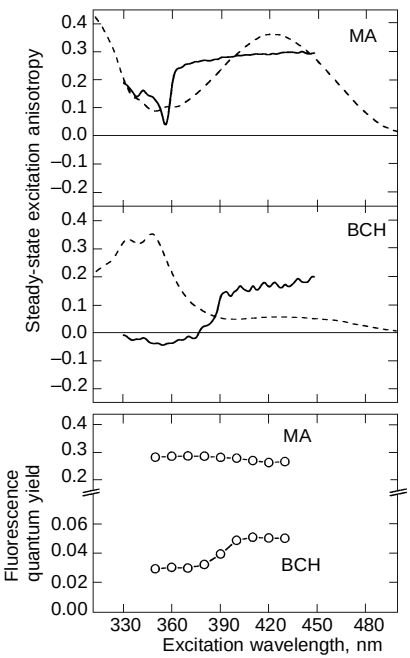


FIG. 2
Steady-state fluorescence excitation anisotropy (full lines) and fluorescence quantum yield (circles) dependence on excitation wavelength for BCH and MA. Anisotropy was measured at 100 K in a rigid 2-methyltetrahydrofurane glass, observation wavelength was 520 nm. Fluorescence quantum yields were determined in DMSO at room temperature. The corresponding absorption spectra of MA and BCH are also indicated (dashed lines)

Time-Resolved Fluorescence Studies

Let us assume that absorption of a photon by the aminopyrene chromophore in BCH results in an excited state that is initially localized at the donor part of BCH. The electronic excitation energy can then be transferred to an electronic state localized at the benzanthrone chromophore, and the dynamics of this process (EET) can be characterized by a single rate constant k_{EET}. Accordingly, BCH excitation into the acceptor absorption band (*i.e.* above 390 nm) should lead to a simple acceptor fluorescence decay, while BCH excitation into the donor absorption band (below 390 nm) and the following EET process should result in an initial rise of acceptor fluorescence determined by the magnitude of k_{EET} and a subsequent monoexponential decay governed solely by localized acceptor photophysics. The ratio of amplitudes of the two components should depend on the excitation wavelength in accordance with donor/acceptor absorption probability. The most simple estimate of k_{EET} could be based on the Forster model of energy transfer. Using that model (though obviously not relevant to the observed fast process in BCH) with the appropriate parameters, *i.e.* size of BCH, experimental donor lifetime, and critical transfer radius R_0 = 27 Å, we estimate $k_{EET(Forster)} \approx 6 \cdot 10^9$ to $2 \cdot 10^{10}$ s^{-1}, this is to say that the expected acceptor fluorescence rise-time would be between 50 and 200 ps.

The fluorescence kinetics measurements with 20 ps time resolution (see TCSPC technique described in Experimental) did not indicate any rising component in BCH emission under any excitation. In order to resolve sub-ps fluorescence kinetics, femtosecond laser excitation and fluorescence up-conversion detection were used as described above. The kinetics depicted in Fig. 3 allows comparison of the BCH fluorescence time profiles during the first ps after excitation with fs-pulses at 403, 386 and 375 nm. There is an obvious excitation wavelength dependence of the fluorescence rising edge, consisting of a very fast component below the time resolution of the experiment with a relative amplitude dependent on excitation wavelength and a slower component on the order of about a picosecond which also varies with the wavelength

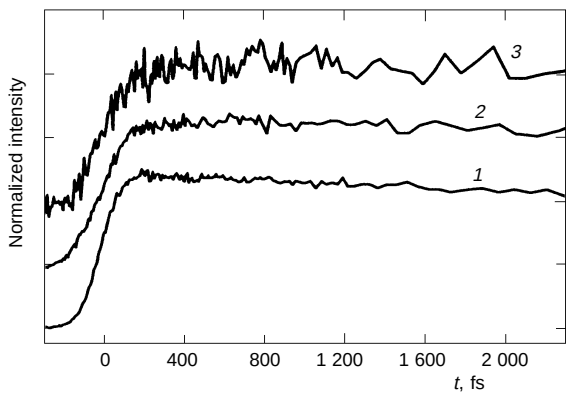


FIG. 3
Comparison of the initial parts (up to 2 ps) of bichromophore BCH fluorescence (detected at 525 nm) measured by fluorescence up-conversion technique using various excitation wavelengths. Curves *1–3* correspond to the excitation wavelengths 403, 386 and 375 nm, respectively

of the laser excitation pulse. The data provide just an upper limit of approximately 220 fs for the fast rise-time. Fluorescence rising part analysis is complicated due to the wavelength dependence of the instrument response function. Furthermore, the presence of a slower component of the rising kinetics suggests that other processes (*e.g.* vibronic or geometrical relaxation and solvation) are involved and they may also influence the dynamics at early times. Whatever its molecular mechanism, the transfer of electronic excitation energy to the acceptor is extremely fast.

Direct observation of electronic excitation energy flow on this time scale is made possible by fluorescence anisotropy measurements, as the emission anisotropy here is determined solely by the mutual orientation of absorption and emission transition moments (the rotation of a molecule as big as BCH takes place on a much longer time scale). The fluorescence anisotropy $r(t)$ at time t is defined by the expression $r(t) = [I_{||}(t) - I_{\perp}(t)]/[I_{||}(t) + 2\, I_{\perp}(t)]$, where $I_{||}(t)$ and $I_{\perp}(t)$ are the fluorescence intensity decays measured with polarization parallel and perpendicular to that of the excitation light. An illustration of corresponding raw experimental data is shown in Fig. 4. A real time picture of acceptor emitting state population can be obtained by comparing the fs fluorescence anisotropy kinetics for BCH with that of model acceptor MA under various wavelength excitation. Kinetics was measured for 403, 392, 386, 383 and 375 nm excitation, results for three of which are depicted in Fig. 5.

Under the 403 nm excitation, the BCH and MA hardly differ in anisotropy kinetics $r(t)$, and during the first few ps their average $r(t)$ values are close to the theoretical limit 0.4.

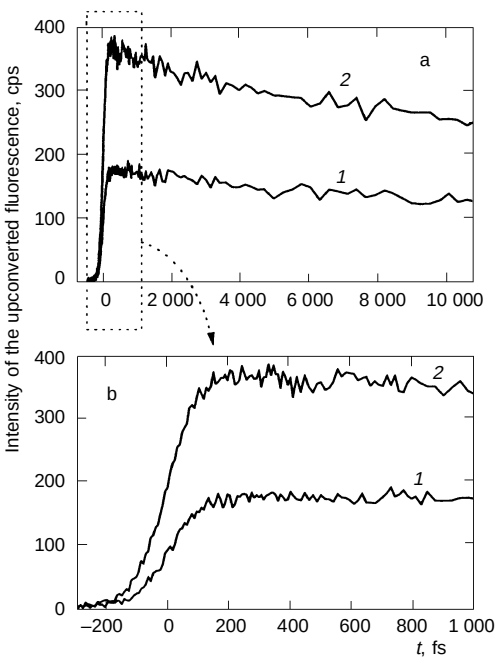


FIG. 4
Illustration of primary experimental data (polarized fluorescence kinetics) measured by fluorescence up-conversion. Fluorescence components having parallel (curve *2*) and perpendicular (curve *1*) polarisations with respect to the excitation light polarization are depicted. The panel a shows the kinetics during the first 10 ps, the panel b shows the first 1 ps of the same decay in more detail (sample: BCH in DMSO, λ_{Exc} = 386 nm, λ_{Em} = 525 nm)

(On a longer time scale $r(t)$ decays due to rotational diffusion.) This lack of depolarization clearly indicates selective excitation of the acceptor chromophore which subsequently fluoresces from its localized state. As discussed earlier, as shorter excitation wavelengths are used, as higher fraction of the excitation energy is absorbed by the donor chromophore of BCH. The absorption transition dipole moments of this pyrene-based chromophore are different in orientation from that of the emitting acceptor chromophore (see Fig. 2, middle panel). This leads to a noticeable fluorescence depolarization appearing on a time scale, which should be indicative of the population rate of the emitting acceptor state (see Fig. 5). Afterwards the anisotropy stays constant (this value can be called "picosecond stationary" anisotropy) on a time scale of 2 to 10 ps. Two features of the results presented in Fig. 5 should be stressed: (i) the decrease of the picosecond stationary anisotropy with decreasing wavelength of excitation is observed for BCH only, while for MA it remains constant, and, (ii) the depolarization process is extremely fast and complete within the first picosecond. Thus, the population of the emitting acceptor state in BCH must take place on a time scale of a few hundred femtoseconds.

The ultrafast fluorescence anisotropy data are summarized in Fig. 6, where the excitation wavelength dependence of the difference between the BCH and MA fluorescence

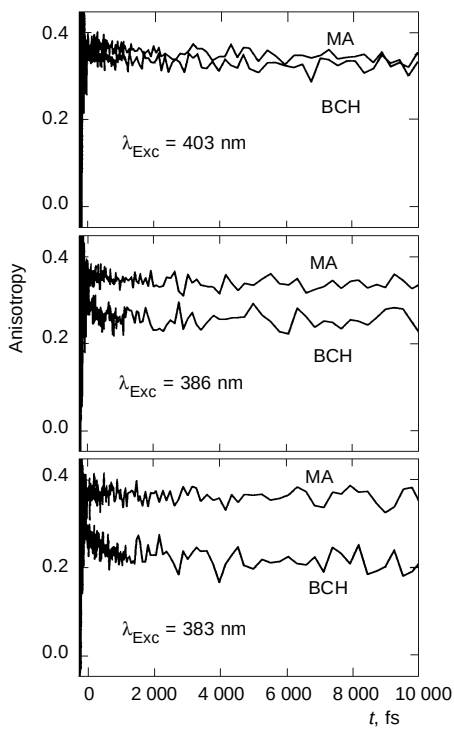


FIG. 5
Comparison of the ultrafast time-resolved fluorescence anisotropy of bichromophore BCH and that of the model acceptor MA compounds. The plotted curves were calculated from primary kinetic data as illustrated in Fig. 4. For both compounds emission at 525 nm was detected; the excitation wavelength is indicated at each plot

anisotropies is depicted (curve *3*) together with estimated time-zero initial anisotropy values (curves *1* and *2*) for both molecules. The excitation wavelengths used here cover the range, where the BCH steady-state anisotropy (see Fig. 2) changes its value in a step-like manner: it can be seen that curve *3* (difference of the BCH and MA "picosecond stationary" anisotropy) exhibits a similar pattern. Both changes occur in the same excitation wavelength region 375–390 nm and provide evidence that donor transition moments are strongly involved in primary excitation. Even more revealing is the time-zero anisotropy (curves *1* and *2* in Fig. 6). The fact that already the initial (bearing in mind the FWHM of the excitation pulse of 150–190 fs) fluorescence anisotropy decreases when the pyrene-based chromophore is excited in BCH clearly shows that noticeable acceptor excited state population has built up within a time period comparable to the duration of the excitation pulse.

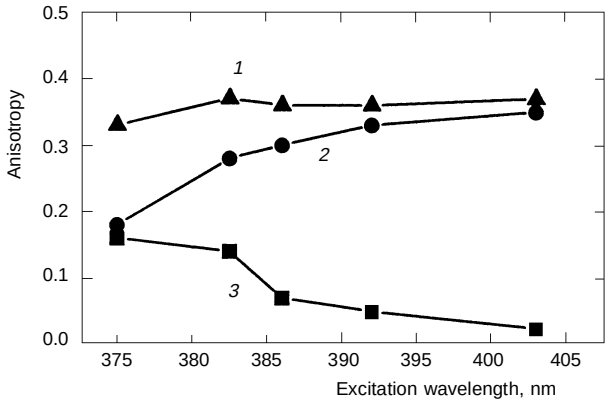


FIG. 6

Summary of the time-resolved anisotropy data analysis for five excitation wavelengths. Curves *1* and *2* show the time-zero anisotropy value estimated by fitting the fs anisotropy kinetics. Curve *3* shows the difference between BCH and MA "picosecond stationary" anisotropies (those anisotropy values after vanishing of the initial sub-ps dynamics and before the onset of rotational depolarization, *i.e.* 2–10 ps after excitation – see Fig. 5)

CONCLUSIONS

Stationary and ultrafast time-resolved fluorescence measurements on the specially designed bichromophoric molecule BCH and corresponding component model compounds MD and MA which closely mimic the photophysical properties of acceptor and donor sub-units in BCH have provided unambiguous evidence for an ultrafast process which leads to practically instantaneous population of the emitting state of the acceptor sub-unit after selective ≈200-fs-excitation of the donor sub-unit. This first direct observation of extremely fast energy transfer in a stiff bichromophore is very surprising

indeed and at this stage one may only speculate about its mechanism. Two conceptually different approaches seem conceivable. There is some spectroscopic evidence that the initially excited donor state is not strictly localized but is vibronically coupled to nearby acceptor states. This interaction could provide an efficient leak into the final emitting state leading to the extremely fast rise-time of the acceptor emission. Alternatively, a sufficiently strong through-bond interaction could also lead to a very efficient electronic excitation energy transfer between localized donor and acceptor excited states. Whether this distinction has a physical foundation or is merely a matter of direction of approach to model the process, has to be clarified by theory and by future experiments using 20 fs coherent excitation which should provide information on the type of coupling involved. No matter what the detailed coupling mechanism is, it provides a route for femtosecond electronic energy flow between two distinct parts of the bichromophore, a fact that by itself should have immediate consequences to the design of molecular electronic devices.

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