Abstract in English

Transient absorption spectroscopy has proven to be a powerful tool to investigate the formation and decay of excited singlet states upon triplet-triplet annihilation, following T-T energy transfer from a selectively excited sensitizer. Thus, upon excitation of benzophenone (BZP) by laser flash photolysis (LFP) at λ = 355 nm in the presence of naphthalene (NPT), a negative band centred at 340 nm has been detected, with growth and decay in the microsecond timescale. It has been assigned to the P-type NPT delayed-fluorescence. In the case of chiral BZP/NPT systems, stereodifferentiation has been observed in the kinetics of the involved photophysical processes.

The triplet state behavior of naphthalene-based pseudopeptides has been investigated in the presence or benzophenone and/or biphenyl, as suitable energy donating chromophores. Their behavior has been compared with that of 1,4-dimethylnaphthalene as model compound. In all cases, the triplet-triplet absorption of naphthalene was detected by transient absorption spectroscopy, upon selective excitation of benzophenone at 355 nm. The kinetics of formation and decay of this species was markedly slower in the pseudopeptides, due to retardation of triplet-triplet energy transfer and exciplex formation. The delayed fluorescence detected in the model naphthalene was absent in the pseudopeptides.

Excited state interactions between *(S)*- or *(R)*-FBP and dThd covalently linked in dyads have been investigated. In both dyads, the

only emitting species was ^{1}FBP*, but with a lower fluorescence quantum yield (ϕ_F) and a shorter fluorescence lifetime (τ_F) than when free in solution. These results indicated that dynamic quenching occured either by electron transfer or *via* exciplex formation, with FBP as the charge donating species. In acetonitrile both mechanisms were favored, while in dioxane exciplex formation was predominating. Isomer *(S)*- displayed lower values of ϕ_F and τ_F than its *(R)*- analog, indicating that the relative spatial arrangement of the chromophores plays a significant role. The triplet quantum yields (ϕ_T) of the dyads were significantly higher than the expectations based solely on ^{1}FBP*-dThd intersystem crossing quantum yields (ϕ_{ISC}), with ϕ_T *(S)*- > ϕ_T *(R)*-. This could be explained in terms of intramolecular charge recombination at the radical ion pairs and/or the exciplexes, which would be again dependent on geometrical factors. The triplet lifetimes (τ_T) of ^{3}FBP*-dThd and free ^{3}FBP* were similar, indicating the lack of excited state interactions at this stage. The FBP-dThd dyads could, in principle, constitute appropriate model systems for the elucidation of the excited state interactions in non-covalent DNA-ligand complexes.

In order to study drug/protein interactions, biphenyl derivatives and tryptophan were covalently linked to provide model dyads. In FBP-Trp dyads, a dramatic fluorescence quenching was observed, and the residual emission was assigned to the Trp unit. This quenching was assigned to an ultrafast ($k > 10^{10}$ s^{-1}) and stereoselective energy transfer from ^{1}FBP* to Trp, with a higher rate constant for the *(R,S)*-diastereomer. At longer timescales, stereoselective quenching of ^{1}Trp*

fluorescence was also noticeable, due to intramolecular electron transfer and/or exciplex formation.

In BPOH-Trp systems, attachment of a hydroxy group at the ortho position of biphenyl resulted in a significant decrease of its singlet energy. A dramatic fluorescence quenching was observed, which displayed a residual emission assigned to the BPOH unit. This result was explained by a stereoselective energy transfer from ^{1}Trp* to BPOH, with a higher rate constant for the *(S,R)*-diastereomer, followed by ^{1}BPOH* quenching due to intramolecular electron transfer and/or exciplex formation. The (*S,R*)-diastereomer exhibited a folded conformation in the solid state, which is in good agreement with the steady-state and time-resolved observations of lower ϕ_F and shorter τ_F values for the (*S,R*)-diastereomer. The fluorescence lifetime was slower in the dyads than in *(S)*-BPOH, confirming a dynamic quenching.

In FBP/HSA systems, the decays at λ_{em}= 310 nm (FBP emission maximum) revealed a configuration-dependent dynamic quenching due to energy transfer, both on the picosecond (FU) and the nanosecond time scales. The kinetic stereodifferentiation was still evident at longer wavelengths (380 nm), where only HSA is emitting. The nature of this quenching was again attributed to a stereoselective electron transfer and/or exciplex formation in the supramolecular systems.

Photophysical characterization of BPOH in aqueous media revealed two emission maxima, one at 332 nm corresponding to ^{1}BPOH* and the other at 414 nm corresponding to phenolate BPO^- emission. In the presence of HSA, a light absorbing ground state

complex BPOH@HSA was detected (maximum at *ca.* 300 nm), whose intensity increased with increasing protein concentration. The fluorescence spectra of *(S)*-BPOH in PBS, after addition of HSA, revealed a progressive diminution of the phenolate band, indicating that excited state deprotonation is disfavored within the hydrophobic protein cavities. A similar trend was observed for *(R)*-BPOH, but the extent of deprotonation was significantly lower for this enantiomer. Addition of increasing amounts of the site II displacement probe *(S)*-IBP to BPOH@HSA led to a significant decrease of the absorption maximum at *ca.* 300 nm and to a recovery of the phenolate emission band at *ca*. 410 nm, which were again configuration-dependent. The transient absorption spectrum of *(S)*-BPOH consisted on a broad band centered at 380 nm, attributed to the first triplet excited state. A dramatic enhancement of the triplet lifetimes within HSA was observed (19 μs within protein *vs*. 1.3 μs in bulk PBS), although no stereodifferentiation was noticed in this case.