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Photoinduced Hole Transfer from the Triplet State in a Porphyrin-Based Donor−Bridge−Acceptor System

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The triplet excited-state deactivation of a gold porphyrin (AuP) in porphyrin-based donor−bridge−acceptor (D−B−A) systems has been studied. The results from room temperature and 80 K measurements are presented. The primary objectives have been to investigate whether electrons/electron holes or excitation energy could be transferred from ^{3}AuP to the appended zinc porphyrin (ZnP) in the dimers. As the bridging chromophores in our D−B−A systems separate the ZnP and AuP moieties by 19 Å edge-to-edge, we do not expect a significant contribution to either electron or energy transfer from a direct (through space) exchange mechanism. This gives us the opportunity to scrutinize how the bridging chromophores influence the transfer reactions. The results show that quenching of ^{3}AuP occurs with high efficiency in the dimers that are connected by fully conjugated bridging chromophores, whereas no quenching is observed when the conjugation of the bridge is broken. We also observed that the decay of ^{3}AuP is complex at temperatures below 110 K. In addition to the two previously published lifetimes on the order of some 10−100 μs, we have found a third lifetime on the nanosecond time scale.

Introduction

The transfer of excitation energy and electrons between photo and/or redox active groups covalently linked by a rigid bridging molecule is an area under intensive investigation.[1−10] The study of intramolecular transfer reactions in donor−bridge−acceptor (D−B−A) systems offers some clear advantages compared to intermolecular transfer between diffusing species separated by solvent molecules. The rigidity of the systems makes it possible to isolate the crucial D−A distance and to constrain the orientation—fundamental parameters that are well-known to affect the rate of the transfer reactions. In the latest decades, though, it has been realized that the bridges possess far more interesting functions than just acting as inert spacers, i.e., keeping the donor and the acceptor moiety at a fixed distance and orientation. The concept by which the bridges contribute to the process by propagating the D−A electronic interaction, thereby accelerating the rate of the transfer reactions, has been formulated as the superexchange mechanism, also called the through-bond mechanism.[11−13] Several groups have put much effort in experimental and theoretical studies in order to gain insight into the set of parameters that determines the influence of the bridge on the transfer reactions.[14−26] One important factor has been shown to be the electronic structure of the bridge. Aiming at a D−B−A system that would promote detailed studies of this feature, we designed a series of porphyrin dimers where the donor porphyrin is covalently attached to the acceptor porphyrin by one of four different bridges.[27,28] To be able to ascribe any change in the transfer reactions throughout the series to the different electronic structure of the bridges, variations of other parameters known to influence the rate of the transfer reactions were minimized. Also, altering the metalation state of the donor and the acceptor porphyrins allows us to focus separately on either electron transfer (ET) or excitation energy transfer (EET). Lately, we have investigated ET in the series of zinc(II)−gold(III) porphyrin dimers shown in Figure 1, and we demonstrated that, upon excitation of the zinc porphyrin donor moiety, ET takes place from the singlet excited state on the subnanosecond time scale in the dimers linked by π-conjugated bridging chromophores. However, when the π-conjugation is broken, no ET occurs (ZnP−OB−AuP).[29] Moreover, the relative efficiencies of ET in the dimers with π-conjugated bridges agree well with what is expected from the superexchange mechanism. The same trend is also observed for EET in the corresponding series of ZnP−RB−H$_2$P dimers.[28−32]

In this work we have extended the studies of ET to include excitation of the AuP electron acceptor moiety. The process, in which the electron acceptor is reduced in its excited state, is often referred to as hole transfer (HT), as it can be regarded as if an electron hole is transferred from the excited electron acceptor to the electron donor. We will present the results from time-resolved as well as steady-state spectroscopic measurements involving the singlet and triplet excited states of both the electron donor (ZnP) and the acceptor (AuP). The focus, however, will be on HT from the AuP excited triplet state.

Experimental Section

Materials. All room temperature measurements were performed with benzonitrile as the solvent. The low-temperature spectra and kinetics were measured with the samples in EPA (a 5:5:2 mixture of diethyl ether, 2-methylbutane, and ethanol). The synthesis and purification of the monomers (ZnP and AuP) and the dimers (ZnP−RB−AuP) are described elsewhere.[29] The

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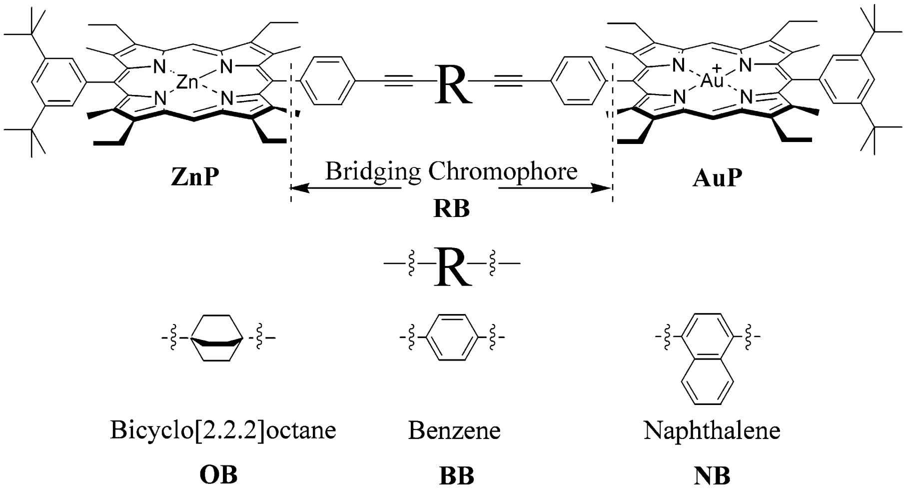

Figure 1. Structure of the compounds studied in this paper. The zinc and gold porphyrin monomers, ZnP and AuP, respectively, are covalently linked together by the bridging chromophores, RB, forming the dimers, ZnP−RB−AuP. The bridging chromophores are varied by changing the central unit, R, to be either bicyclo(2.2.2)octane (O), benzene (B), or naphthalene (N). The monomers covalently linked to the bridging chromophores, AuP−RB and ZnP−RB, are referred to as the reference substances.

reference compounds AuP−RB were prepared through gold insertion into the free base analogue H_2P−RB. These free base precursors were prepared as previously reported.[33] In a typical experiment for gold insertion, a solution of the free base precursor H_2P−RB (1 equiv), $[Au(tht)_2]BF_4$ (4.5 equiv), and 2,6-lutidine (3 equiv) in $CHCl_3$ was heated to reflux for 1 h. The solvent was evaporated. The residue was dissolved in CH_2Cl_2 and added to a chromatographic column (Al_2O_3, grade III). Residues of the free base porphyrin were removed by elution with pure CH_2Cl_2. The gold porphyrin was collected by elution with 2% MeOH in CH_2Cl_2. Recrystallization of the gold porphyrin from CH_2Cl_2/hexane gave AuP−RB of high purity in a total yield of 23−35%, nonoptimized.

AuP−OB: ^{1}H NMR δ 1.52 (s,18 H, *t*-Bu), 1.83 (t, $J = 7.6$ Hz, 12 H, $-\mathrm{CH_2}\mathit{CH}_3$), 2.04 (m, 12 H, BCO−$CH_2$), 2.57 (s, 6 H, pyrrole-CH_3), 2.65 (s, 6 H, pyrrole-CH_3), 4.12 (m, 8 H, $-\mathit{CH}_2\mathrm{CH_3}$), 7.29 (m, 3 H, ArH), 7.41 (m, 2 H, ArH), 7.86 (s, 2 H, ArH), 7.88 (d, $J = 8$ Hz, 2 H, ArH), 7.94 (s, 1 H, ArH), 7.98 (d, $J = 8$ Hz, 2 H, ArH), 10.63 (s, 2 H, *meso*).

AuP−NB: ^{1}H NMR δ 1.53 (s,18 H, *t*-Bu), 1.83 (m, 12 H, $-\mathrm{CH_2}\mathit{CH}_3$), 2.58 (s, 6 H, pyrrole-CH_3), 2.73 (s, 6 H, pyrrole-CH_3), 4.14 (m, 8 H, $-\mathit{CH}_2\mathrm{CH_3}$), 7.44 (m, 3 H, ArH), 7.68−7.95 (m, 9 H, ArH), 8.14 (d, $J = 8$ Hz, 2 H, ArH), 8.18 (d, $J = 8$ Hz, 2 H, ArH), 8.50 (d, $J = 8.4$ Hz, 1 H, ArH), 8.64 (d, $J = 8.4$ Hz, 1 H, ArH), 10.66 (s, 2 H, *meso*).

AuP−BB: ^{1}H NMR δ 1.53 (s,18 H, *t*-Bu), 1.85 (t, $J = 7.6$ Hz, 12 H, $-\mathrm{CH_2}\mathit{CH}_3$), 2.57 (s, 6 H, pyrrole-CH_3), 2.68 (s, 6 H, pyrrole-CH_3), 4.13 (m, 8 H, $-\mathit{CH}_2\mathrm{CH_3}$), 7.39 (m, 3 H, ArH), 7.58 (m, 2 H, ArH), 7.63 (d, $J = 8$ Hz, 2 H, ArH), 7.70 (d, $J = 8$ Hz, 2 H, ArH), 7.89 (s, 2 H, ArH), 7.93 (s, 1 H, ArH), 8.04 (d, $J = 8$ Hz, 2 H, ArH), 8.13 (d, $J = 8$ Hz, 2 H, ArH), 10.63 (s, 2 H, *meso*).

The structures of the studied compounds are shown in Figure 1.

Spectroscopic Measurements. Ultraviolet−visible ground-state absorption spectra were measured on a Shimadzu UV2100U UV−vis spectrometer. Steady-state emission spectra were measured using a SPEX Fluorolog τ2 spectrofluorometer. Time-resolved phosphorescence measurements on the microsecond time scale were performed by xenon lamp pulsed excitation followed by gated phosphorescence detection using a SPEX 1934D3 phosphorimeter. On the nanosecond time scale, the phosphorescence lifetimes were measured by time-correlated single photon counting (SPC). The samples were excited at 400 nm by the frequency-doubled output from a Ti:sapphire laser (Spectra Physics, Tsunami) pumped by a diode-pumped CW solid-state laser (Spectra Physics, model Millennia V*s*). The repetition rate was pulse-picked to 40 kHz before sample excitation. The emitted photons were registered by a cooled microchannel plate detector (model C3360) from Hamamatsu. The instrument response function was estimated to be 25 ps from light scattering detection at the excitation wavelength. Nanosecond transient absorption measurements were made with excitation from an Opotek optical parametric oscillator pumped by the third harmonic of a Continuum Surelight Nd:YAG laser. The pulse width was ~5 ns, and the repetition rate was 10 Hz. The detection portion of the spectrometer has been described elsewhere.[34] To minimize interference from triplet annihilation and self-quenching and to avoid kinetic distortions caused by inhomogeneities in the sample distribution, the ground-state absorption at the excitation wavelength was adjusted to 0.05 and the T_1-T_n absorption was kept below 0.15.[35] Fluorescence decay measurements at room temperature were performed on $\sim 1 \times 10^{-5}$ M solutions by SPC. The excitation source was a cavity-dumped Coherent 700 dye laser pumped by a frequency-doubled Coherent Antares 76s Nd:YAG laser.[36] The instrument response function was 35 ps, as measured at the excitation wavelength for each decay experiment with Ludox AS-40 scattering solution. The femtosecond transient absorption apparatus consists of a kilohertz pulsed laser source and a pump−probe optical setup. The laser pulse train was provided by a Ti:sapphire regenerative amplifier (Clark-MXR, model CPA-1000) pumped by a diode-pumped CW solid-state laser (Spectra Physics, model Millennia V). The typical laser pulse was 100 fs at 790 nm, with a pulse energy of 0.9 mJ at a repetition rate of 1 kHz. Most of the laser energy (80%) was used to pump an optical parametric amplifier (IR-OPA, Clark-MXR). The excitation pulse was sent through a computer-controlled optical delay line. The remaining laser output (20%) was focused into a 1.2 cm rotating quartz plate to generate a white light continuum. The continuum beam was further split into two identical parts and used as the probe and reference beams. The probe and reference signals were focused onto two separated optical fiber bundles coupled to a spectrograph (Acton Research, model SP275). The spectra were acquired on a dual diode array detector (Princeton Instruments, model DPDA-1024).[37] Spectral dispersion was corrected for using the optical Kerr effect in CS_2. Prior to transient absorption and fluorescence decay measurements at room temperature, all samples were carefully deoxygenated by 30 min argon-bubbling or degassed by six freeze−pump−thaw cycles to a final pressure of about 10^{-4} Torr. Low-temperature measurements were done in a nitrogen-cooled cryostat (Oxford Instruments) equipped with a temperature regulator.

Results

The primary purpose of this work has been to investigate the triplet excited-state deactivation of AuP in the different ZnP−RB−AuP dimers at room temperature and at 80 K. The corresponding decay kinetics of the singlet excited state of ZnP have previously been characterized.[29] The focus here is on the process in which AuP in its triplet excited state possibly accepts an electron from ZnP. This process can be regarded as either electron transfer (ET) from ZnP to ^{3}AuP or, alternatively, hole transfer (HT) from ^{3}AuP to ZnP.

The results section is organized as follows: First, we give a short description of the design criteria of the dimers, followed by a spectroscopic characterization of the ground-state absorption and emission properties of the compounds studied. Second, we present the energy level diagram of the various excited and charge shifted[38] states involved in the overall deactivation process of the dimers. Then, the results from time-resolved emission and transient absorption measurements at room temperature are presented. These data are used to quantify the rates of the ET/HT reactions between the porphyrin moieties in the dimers at room temperature. The lifetimes of the charge shifted states, ZnP$^{\bullet +}$−RB−AuP$^{\bullet}$, were also determined. Finally, the results from steady-state and time-resolved measurements at 80 K are presented. Here, we show that the quenching of the triplet excited state of AuP is decreased by more than 5 orders of magnitude compared to room temperature. The origin of the quenching at 80 K is discussed in terms of HT vs EET.

Design. The D−B−A systems investigated in this study consist of a zinc(II) porphyrin (electron donor) and a gold(III) porphyrin (electron acceptor) at 25 Å center−center distance (see Figure 1). The distance and the orientation between the porphyrin subunits are fixed by covalently linking them by one of three different bridging chromophores. The dimers were designed to answer questions about the influence of the bridges on the rate of photoinduced ET. Variation of all other parameters that might affect the ET process should therefore be minimized through the series of dimers. The different design criteria and the strategy used to fulfill the conditions have been described.[20]

Ground-State Absorption and Emission Spectra. Figure 2 shows the Q-band region of the room-temperature absorption spectra of ZnP and AuP and the corresponding emission spectra recorded at 80 K. Absorption maxima are found at 518 and 553 nm for AuP and at 544 and 577 nm for ZnP. Fluorescence band maxima from ZnP are observed at 577 and 637 nm, together with the phosphorescence maxima at 719 and 802 nm. AuP is nonluminescent at room temperature but shows phosphorescence at 80 K with peaks located at 683, 692, 715, and 760 nm. The observed bands are in agreement with earlier reported data on similar porphyrins.[39−43] The absorption spectra were recorded on equimolar samples, which allows a direct comparison between the spectra, whereas the emission spectra are normalized. At 518 nm, $\epsilon(\mathrm{AuP})/\epsilon(\mathrm{ZnP}) = 4.8$, and about 85% of the light is absorbed by AuP in the dimers. The corresponding value for ZnP with excitation at 577 nm is 75%. Excitation spectra of the monomers, ZnP and AuP, recorded with the emission wavelength in the fluorescence and phosphorescence bands do not show significant deviations from the respective absorption spectra. The absorption spectra of the dimers in the Q-band region are very close to a superposition of the ZnP and AuP monomers, although some deviations are observed in the Soret-band region (not shown).[29] This signals that there is no significant electronic coupling between the different chromophores in the ground state.

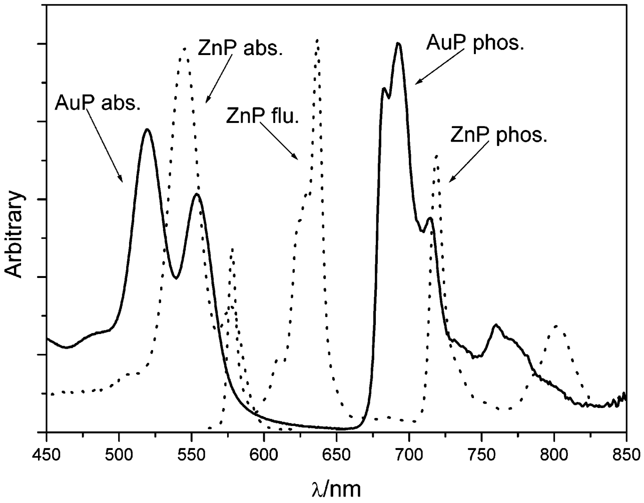

Figure 2. Ground-state absorption and emission spectra of AuP (—) and ZnP (• • •). The absorption spectra are recorded at room temperature in benzonitrile while the emission spectra are recorded in EPA at 80 K.

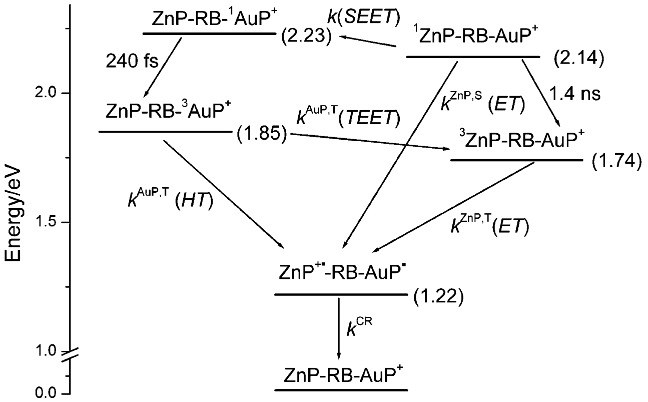

Figure 3. Energy level diagram showing the energies of the excited and charge shifted states together with the relevant transfer processes studied in this work. Although SEET ^{1}ZnP → ^{1}AuP is thermodynamically unfavorable, the overlap integral, *J*, is nonzero, and thus, a contribution from the Förster mechanism is expected. Please note that the Coulombic stabilization term has been omitted in the determination of the charge shifted state energy, since the ET and HT reactions have the character of a charge shift.

Energetics. Figure 3 shows the energies of the relevant states involved in the various photophysical processes. The energies of the singlet and triplet excited states were determined from the 0−0 transitions, as estimated from the absorption and emission spectra. The energy of the charge shifted state was estimated from the redox potentials of the species involved in the ET processes. The details of the cyclic voltammetric measurements are described in ref 29.

Time-Resolved Fluorescence Measurements at Room Temperature. The room temperature singlet lifetimes of the ZnP monomer, τ_f^0, and the dimers, τ_f, were measured by SPC in benzonitrile solution. The samples were excited at 577 nm, and the decays were probed at 650 nm. Although AuP accounts

TABLE 1: Room Temperature Singlet Lifetimes of ZnP (τ_f) and Triplet Lifetimes of AuP Monomer (τ_T) Together with the Corresponding Rate Constants of ET ($k^{ZnP,S}$) and HT ($k^{AuP,T}$)[a]

	ZnP	AuP	AuP−OB	AuP−BB	AuP−NB	ZnP−OB−AuP	ZnP−BB−AuP	ZnP−NB−AuP
τ_f/ns	1.40					1.24	0.205	0.134
$k^{ZnP,S}$/s^{-1}						9.2×10^7 [b]	4.2×10^9	6.7×10^9
$\tau_T{}^c$/ns		0.472	0.470	0.473	0.475	0.472	0.438	0.360
$k^{AuP,T}$/s^{-1}						≈ 0	1.7×10^8	6.7×10^8

[a] The lifetimes of ZnP in all compounds are estimated from SPC measurements. χ^2 varied between 1.01 and 1.19. The corresponding AuP lifetimes are determined by picosecond transient absorption measurements. In the evaluation of the AuP lifetimes, the ZnP lifetimes from the SPC measurements were included and fixed, as ^{1}ZnP absorbs in the same wavelength region as ^{3}AuP. [b] The observed quenching rate constant for ZnP−OB−AuP has been shown to be SEET from ^{1}ZnP to AuP.[29] [c] The experimental uncertainties of the lifetimes are estimated to be ±10 ps.

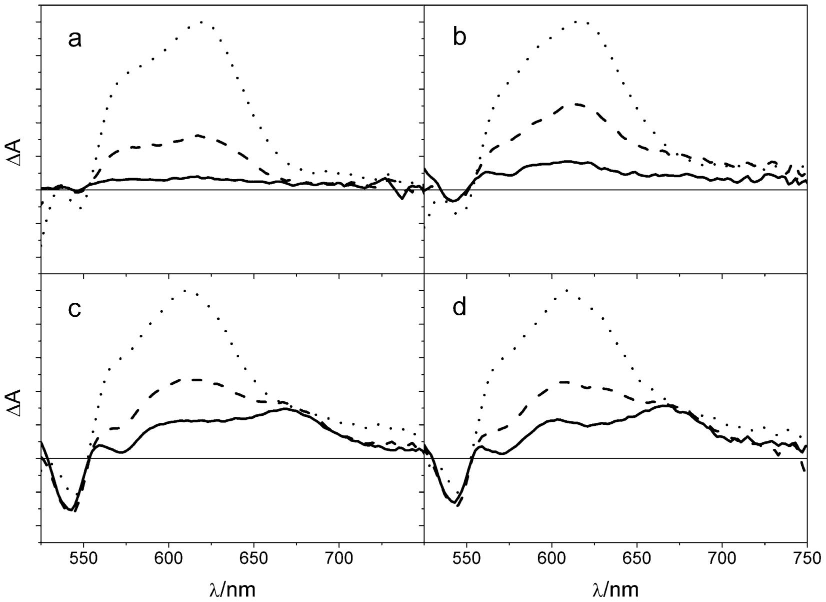

Figure 4. Transient absorption spectra at delay times of 50 ps (• • •), 500 ps (— — —), and 1.5 ns (—). All samples were excited at 518 nm. (a) AuP monomer, (b) ZnP−OB−AuP, (c) ZnP−BB−AuP, and (d) ZnP−NB−AuP. The peak at 680 nm in (c) and (d) clearly shows that ZnP$^{\bullet+}$ is being formed.

for 25% of the photons absorbed in the dimers at 577 nm, the emission is ascribed exclusively to ZnP as AuP is nonluminescent at room temperature.[41,44] The resulting lifetimes are shown in Table 1. In comparing the lifetime of the ZnP monomer with the corresponding values in the dimers, a substantial decrease is seen in the ZnP−NB−AuP and ZnP−BB−AuP dimers, whereas the effect is less pronounced in the ZnP−OB−AuP dimer. This is the same trend as described in ref 29, where similar measurements were performed in a series of other solvents. The quenching rates of the ZnP singlet excited state in the dimers, $k^{ZnP,S}$, are calculated according to

$$k^{ZnP,S} = \frac{1}{\tau_f} - \frac{1}{\tau_f^0} \qquad (1)$$

The resulting rate constants for the three dimers are shown in Table 1.

Picosecond Transient Absorption Measurements. Picosecond time-resolved absorption experiments were performed to investigate the excited-state deactivation of AuP. Figure 4a shows the time evolution of the transient absorption spectrum after excitation of the AuP monomer at 518 nm. The broad absorption band with a maximum around 620 nm is characteristic of ^{3}AuP.[39,40,42,43,45] By probing the rise time of the transient T_1-T_n absorption at 620 nm, which is equivalent to the rate of intersystem crossing (isc), S_1-T_1, the singlet lifetime was determined to be 240 fs.[44] The subsequent depopulation of the triplet excited state was probed by monitoring the decay curve at longer times. The decay curve is well described in terms of a single exponential with a lifetime, τ_T^0, of 472 ps, although the fit is slightly improved by including a short-lived component of about 3 ps. The lifetime agrees well with previous literature values.[39] It is also worth noticing that the band shape does not change with time to any large extent; in particular, the maximum is located at 620 nm irrespective of delay time. Also, the lifetimes for the AuP reference substances, AuP−RB, are within experimental uncertainties (±10 ps) the same as for the monomer. The corresponding spectra of the dimers are shown in Figure 4b−d. Comparing the time evolution of the spectrum of ZnP−OB−AuP (b) with the two other dimers, ZnP−BB−AuP (c) and ZnP−NB−AuP (d), it is obvious that the spectral features change drastically with time in the two latter dimers but not in the former. The most notable feature is the appearance of a band at about 680 nm, which signals that ZnP$^{\bullet+}$ is being formed.[43,46,47] In a similar series of measurements, where the samples were excited at 577 nm (mainly ZnP excitation), the spectral evolution suggests that the formation of ZnP$^{\bullet+}$ is also coupled to the decay of ^{1}ZnP. The triplet lifetime of AuP in the dimers, τ_T, was determined by probing the decay at 620 nm, and the results are presented in Table 1. The trend is the same as was observed for the singlet lifetime of ZnP. There is significant shortening of the lifetimes in the ZnP−NB−AuP and ZnP−BB−AuP dimers, whereas no quenching occurs in the ZnP−OB−AuP dimer. The rate constants for the quenching process of AuP triplet excited state in the dimers, $k^{AuP,T}$, were determined from eq 1 and are collected in Table 1.

Nanosecond Transient Absorption Measurements at Room Temperature. To determine the triplet lifetime of ZnP in the

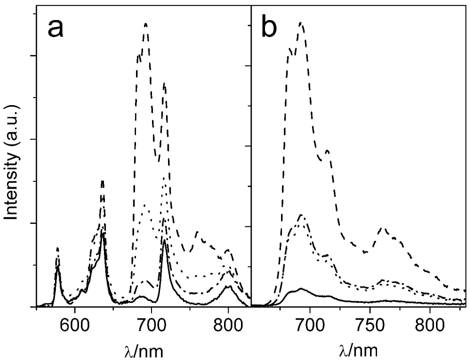

Figure 5. (a) Steady-state emission spectra at 80 K for ZnP−NB−AuP (—), ZnP−BB−AuP (− · −), ZnP−OB−AuP (· · ·), and a 1:1 mixture of ZnP and AuP (− − −). (b) Steady-state emission spectra at 80 K for AuP−NB (—), AuP−BB (− · −), AuP−OB (· · ·), and AuP monomer (− − −). The absorption of the samples was matched at the excitation wavelength 518 nm.

monomer and in the dimers, nanosecond transient absorption measurements were performed at room temperature. In addition, if the rate of charge recombination (CR) corresponds to some 10 ns or longer, the lifetimes of the charge shifted states in the dimers could also be determined. As both the singlet and the triplet lifetime of AuP and the singlet lifetime of ZnP at room temperature are much shorter than the time resolution of the instrument (about 10 ns), we would expect to see contributions only from ^{3}ZnP and ZnP$^{\bullet +}$/AuP$^{\bullet}$ in the transient decay curves. Upon excitation at either 518 nm (AuP) or 577 nm (ZnP) a fast decay in the early part of the transients of both the ZnP−NB−AuP and ZnP−BB−AuP dimers was observed at wavelengths around 450 nm, where ZnP$^{\bullet +}$ absorbs strongly.[47] The lifetimes were determined to be 30 and 50 ns, respectively. It is also interesting to note that the lifetimes do not depend on the excitation wavelength. In contrast, the corresponding transients for the ZnP−OB−AuP dimer and the ZnP monomer did not show any trace of a fast decay but contained all the expected features from the decay of ^{3}ZnP.[48] Hence, we ascribe the 30 and 50 ns lifetimes to the charge shifted states. In an attempt to determine whether ^{3}ZnP is involved in any ET reactions or, more specifically, whether the charge shifted state can be populated from ^{3}ZnP, we tried to estimate the triplet lifetimes of ZnP in the dimers. It turned out, however, that the signals from ^{3}ZnP in the transient decays were too weak to allow any good estimates of the lifetimes. This is a result of the efficient quenching of ^{1}ZnP in the dimers; the effective quantum yield of triplet formation is less than 5% in the ZnP−NB−AuP dimer.

Steady-State Emission Measurements at 80 K. Figure 5a shows the emission spectra of ZnP−NB−AuP, ZnP−BB−AuP, ZnP−OB−AuP, and a 1:1 mixture of ZnP and AuP monomers. The spectra were recorded using optically matched solutions, so that the emission intensities are directly comparable. The fluorescence from ZnP is seen between 570 and 660 nm with maxima at 577 and 637 nm. The extent of ZnP fluorescence quenching in the dimers varies in the following order: ^{1}ZnP−NB−AuP (most quenched) > ^{1}ZnP−BB−AuP > ^{1}ZnP−OB−AuP (least quenched). Comparing the relative intensities at 692 nm, where the emission is ascribed almost exclusively to AuP phosphorescence, it is seen that the emission is quenched in the dimers. The order of AuP quenching follows the same trend as for the ZnP fluorescence, i.e., ZnP−NB−^{3}AuP (most quenched) > ZnP−BB−^{3}AuP > ZnP−OB−^{3}AuP (least quenched). The quenching in the ZnP−NB−AuP and ZnP−BB−AuP dimers is too efficient to allow an accurate quantification of the phosphorescence intensities, and we can only draw qualitative conclusions from these measurements. The ZnP phosphorescence maximum at 719 nm overlaps the emission from AuP. A direct comparison between the total emission intensities at 719 nm would therefore not be adequate in order to estimate the contribution from ZnP. However, by fitting the four spectra to the component spectra of ZnP and AuP (not shown), it can be seen that the variation in the ZnP phosphorescence intensity virtually parallels the variation in the corresponding fluorescence intensity. Thus, the observed intensity variation is ascribed to a decrease in the initial ^{3}ZnP population and not to additional quenching of ^{3}ZnP in the dimers.

Figure 5b shows the corresponding emission spectra of the AuP monomer and the AuP reference substances AuP−OB, AuP−BB, and AuP−NB. Again, the absorption was matched at the excitation wavelength, which allows direct comparison of the emission intensities. Unexpectedly, the phosphorescence quantum yield decreases more than 10 times comparing the AuP monomer with AuP−NB. A significant decrease in the phosphorescence intensity is also observed for AuP−OB and AuP−BB. This is indeed surprising, as both HT and EET to the bridges in fluid benzonitrile are thermodynamically unfavorable by 0.19 and 0.32 eV, respectively, for AuP−NB along with 0.37 and 0.63 eV for AuP−BB. In addition, the phosphorescence measurements were actually performed in a rigid glass at 80 K, where the energies of the charge shifted states AuP$^{\bullet}$−RB^{+} should be even higher due to the restricted ability of the solvent molecules to reorient around the new charge distribution. We also know from the picosecond transient absorption measurements at room temperature that the ^{3}AuP chromophore is not quenched by attaching any of the RB bridges, indicating that no observable HT/TEET occurs. However, this last result cannot be directly translated to the situation at 80 K, where the lifetime of ^{3}AuP is increased by up to 5 orders of magnitude (vide infra).

Time-Resolved Measurements at 80 K. To quantify the quenching of ^{3}AuP in the dimers and further investigate the unexpected difference in phosphorescence intensities for AuP and AuP−RB, time-resolved gated phosphorescence measurements were performed. The samples with matched optical densities were excited at 518 nm, and the emission was monitored at four wavelengths between 686 and 692 nm. The normalized, averaged decay curves for the ZnP−RB−AuP dimers and the corresponding AuP−RB reference substances are shown in Figure 6. The kinetics of ^{3}AuP in the reference substances as well as in the dimers is clearly biexponential on this time scale, an observation made by several groups earlier.[39,41,42,45] The emission decays were therefore fitted to the following expression

$$I(t) = \alpha_B \exp(-t/\tau_B) + \alpha_C \exp(-t/\tau_C) + I_\infty \qquad (2)$$

where α are the preexponential factors, τ are the lifetimes, and I_∞ represents the contribution from ^{3}ZnP (80 ms at 80 K) where appropriate. The lifetimes are shown together with the averaged preexponential factors in Table 2. The rate constants of the quenching processes, $k^{\mathrm{AuP,T}}$, are each calculated according to

$$k^{\mathrm{AuP,T}} = \frac{1}{\tau_p} - \frac{1}{\tau_p^0} \qquad (3)$$

where τ_p^0 and τ_p refer to the phosphorescence lifetimes of AuP in the reference substances and in the dimers, respectively. It is worth emphasizing that the comparisons are made between the AuP−RB reference substances and the corresponding dimers. A comparison between the AuP monomer and the dimers would not be fair, since the decay properties of AuP and AuP−RB

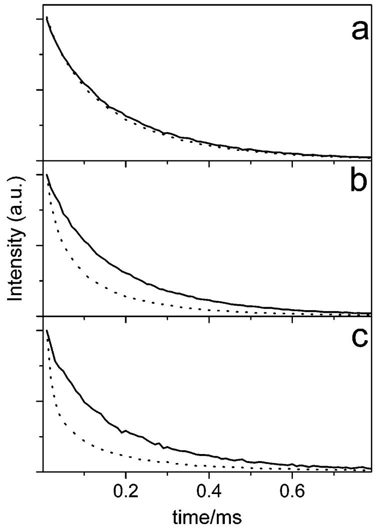

Figure 6. Normalized phosphorescence decays at 80 K for AuP in (a) AuP−OB (—) and ZnP−OB−AuP (• • •), (b) AuP−BB (—) and ZnP−BB−AuP (• • •), and (c) AuP−NB (—) and ZnP−NB−AuP (• • •). The first 10 μs of the decays is discarded due to detection gating. On this time scale, the decays are clearly biexponential.

differs significantly (see Table 2 and Figure 5). Still, it is obvious that the moderate quenching of ^{3}AuP in the AuP−RB reference substances compared to the AuP monomer, as judged by comparing solely the triplet lifetimes (see Table 2), does *not* account for the drastic decrease of the steady-state phosphorescence intensity in the reference compounds (see Figure 5b). However, by examining the preexponential factors of the AuP phosphorescence in the time-gated experiments, it is seen that the initial phosphorescence intensities, represented by the sum of the preexponential factors, $\alpha_B + \alpha_C$, and hence the initial population of the triplet states, decrease in the following order: AuP > AuP−BB > AuP−OB > AuP−NB. In fact, this variation is almost identical to the variation in the steady-state emission intensities. A corresponding comparison between the measurements on the series of dimers shows that the variations in the $\alpha_B + \alpha_C$ values and the equivalent steady-state phosphorescence intensities virtually parallel each other. This indicates that quenching occurs in the reference substances as well as in the dimers prior to the population of the states responsible for the phosphorescence detected in the time-gated experiments.

Monitoring the emission at 719 nm (emission maxima of ZnP phosphorescence), similar measurements were performed to determine the lifetimes of ^{3}ZnP. Comparing the lifetime of the ZnP monomer, (60 ms) with the corresponding lifetimes in the dimers (59, 63, and 57 ms for AuP−OB−ZnP, AuP−BB−ZnP, and AuP−NB−ZnP, respectively), it is seen that the variation of the lifetimes falls within the experimental errors. It is also worth mentioning that there are no significant deviations in the decay of ^{3}ZnP in the ZnP monomer and in the ZnP−RB reference substances.[48]

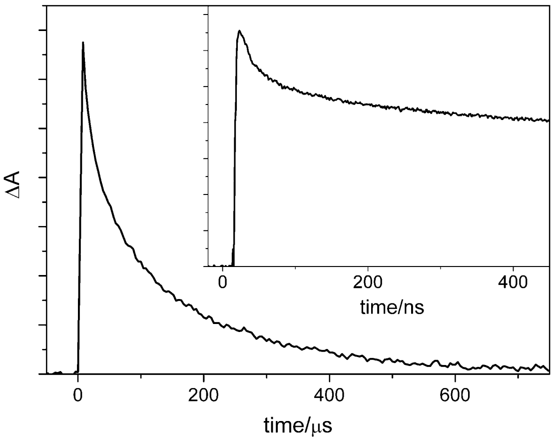

Figure 7. Transient T_1−T_n absorption decay of AuP at 80 K recorded at 450 nm. Inset: the corresponding decay at shorter times, in which the third, ≈18 ns lifetime is seen. Please note the different time scales.

To investigate the low-temperature decay characteristics of ^{3}AuP at shorter times, nanosecond transient absorption measurements were performed on the AuP monomer. The transient recorded at 450 nm, where ^{3}AuP absorbs strongly, with the shortest time window is shown in Figure 7 (inset). The fast decay in the early part of the transient clearly signals the presence of a short-lived state, with a lifetime of about 18 ns. Using a longer time window, the two long-lived states were also probed. The resulting lifetimes, 60 and 224 μs, are close to what was found in the time-gated phosphorescence measurements (54 and 196 μs). The presence of a short lifetime leads to a situation in which the overall decay of ^{3}AuP at 80 K can be fit with three exponential components. It is also worth mentioning that the triexponential character of the decay was retained at 110 K, i.e., well above the glass transition temperature of the solvent.

To further establish the presence of, and to get better estimates of, the short lifetime of ^{3}AuP in the monomer, the reference substances, and in the dimers, SPC measurements were performed at 80 K. The emission was recorded at four different wavelengths around the AuP phosphorescence maxima (690−696 nm) and at four wavelengths around the ZnP fluorescence maxima (634−640 nm). The decays of the emission between 690 and 696 nm were fitted to a biexponential expression similar to eq 2. The biexponential character is most likely a result of contributions from both ZnP fluorescence and AuP phosphorescence in the wavelength region, as the shortest lifetime is well described by the observed lifetime of ^{1}ZnP. The short lifetime of ^{3}AuP (τ_A) varies according to the following: about 18 ns for the AuP monomer, AuP−OB reference substance, and AuP−OB−ZnP, along with about 5 ns for AuP−BB, AuP−NB, and the corresponding dimers (see Table 2). The variations

TABLE 2: Lifetimes (τ), Preexponential Factors (α), and Quenching Rate Constants ($k^{AuP,T}$) for the Triplet Species of AuP at 80 K

	AuP	AuP−OB	AuP−BB	AuP−NB	AuP−OB−ZnP	AuP−BB−ZnP	AuP−NB−ZnP
τ_A/ns	18	18	5.5	5.6	19	5.3	5.3
τ_B/μs	54	44	57	45	42	28	14
α_B	0.18	0.05	0.09	0.02	0.08	0.04	0.02
τ_C/μs	196	200	200	196	195	148	140
α_C	0.82	0.20	0.25	0.04	0.18	0.03	0.01
$\alpha_B + \alpha_C$	1	0.25	0.34	0.06	0.26	0.07	0.03
$k_A^{AuP,T}$/s^{-1}					$< 10^7$	$< 10^7$	$< 10^7$
$k_B^{AuP,T}$/s^{-1}					≈0	1.8×10^4	4.9×10^4
$k_C^{AuP,T}$/s^{-1}					≈0	1.8×10^3	2.0×10^3

in lifetimes between the AuP−RB reference substances and the corresponding AuP−RB−ZnP dimers are too small to signal any significant quenching due to ET/HT or EET on the nanosecond time scale. The best we can do is to set a highest limit quenching rate constant to 10^7 s^{-1}. However, the presence of a lifetime on the nanosecond time scale in all the compounds studied is additional evidence that the decay of ^{3}AuP is triexponential at 80 K.

Discussion

Electron and Hole Transfer at Room Temperature. In a previous study, it was shown that ET ^{1}ZnP−RB−AuP$^+$ → ZnP$^{\bullet+}$−RB−AuP$^\bullet$ dominates the deactivation of ^{1}ZnP in the ZnP−BB−AuP and ZnP−NB−AuP dimers at room temperature.[29] From the room temperature SPC measurements performed in this study, it is seen that the quenching of ^{1}ZnP agrees well with that expected from ref 29. Also, the results from picosecond transient absorption measurements show that ZnP$^{\bullet+}$ is formed in ZnP−BB−AuP and ZnP−NB−AuP with the same rate as ^{1}ZnP depopulates. This is clear evidence that ET occurs from the singlet excited state of ZnP. As discussed in ref 29, the contribution from Förster type singlet energy transfer (SEET) from ^{1}ZnP to AuP is expected to be about 1×10^8 s^{-1} in polar solvents. Comparing this value with $k^{\mathrm{ZnP,S}}$ in Table 1 shows that the quenching of ^{1}ZnP in ZnP−OB−AuP quantitatively is accounted for by SEET. Another observation in favor of this point is that no trace of ZnP$^{\bullet+}$ is seen in the transient absorption spectra of ZnP−OB−AuP upon excitation of ZnP. Therefore, we can establish that virtually no ET occurs from ^{1}ZnP in ZnP−OB−AuP whereas it is the dominating deactivation channel in ZnP−BB−AuP and ZnP−NB−AuP ($k^{\mathrm{ZnP,S}} = 4.2 \times 10^9$ and 6.7×10^9 s^{-1}, respectively).

Upon excitation at 518 nm, where AuP accounts for 85% of the absorbed light in the dimers, ^{3}AuP is populated by rapid intersystem crossing.[44] As the singlet lifetime of the AuP monomer is as short as 240 fs, we do not expect long-range electron or energy transfer to contribute significantly to the deactivation of ^{1}AuP in the ZnP−RB−AuP dimers. Consequently, the starting point of HT or EET is ^{3}AuP. The results from the picosecond transient absorption measurements shown in Figure 4 (excitation of mainly AuP) and Table 1 contain the same relevant features as described for ZnP excitation. In the ZnP−OB−AuP dimer, neither quenching of ^{3}AuP nor formation of ZnP$^{\bullet+}$ is seen, and so we conclude that the rates for HT/EET in this dimer is too slow to compete with the intrinsic deactivation of ^{3}AuP. Conversely, in the ZnP−BB−AuP and ZnP−NB−AuP dimers, ^{3}AuP is quenched and the 680 nm band of ZnP$^{\bullet+}$ appears in the spectra as ^{3}AuP depopulates. Although the decrease in lifetime for ^{3}AuP in the ZnP−BB−AuP dimer, as judged from the lifetimes in Table 1, is quite small, it is most likely that quenching occurs since fitting the transient decays of ZnP−BB−^{3}AuP with a fixed lifetime of 473 ps (corresponding to unquenched ^{3}AuP−BB), results in residuals with *far worse* quality.

The formation of ZnP$^{\bullet+}$ after excitation at 518 nm could, in principle, originate from directly excited ZnP (15% of the absorbed light is ascribed to ZnP at 518 nm) and subsequent ET from ^{1}ZnP. The ^{3}AuP quenching could then potentially be a result of TEET ^{3}AuP → ^{3}ZnP. However, the ZnP$^{\bullet+}$-induced signal in the nanosecond transient absorption measurements revealed that the yield of ZnP$^{\bullet+}$ formation is about twice as high upon excitation of ZnP−NB−AuP at 577 compared to 518 nm. This is consistent with a situation where the observed quenching of ^{3}AuP stems from HT, whereas the expected yield of ZnP$^{\bullet+}$ would be about 5 times higher upon excitation at 577 compared to 518 nm in the case of TEET being the origin of the quenching. This is clearly not observed.

As for the properties of the charge shifted states, the lifetimes were determined to be 30 and 50 ns for ZnP−NB−AuP and ZnP−BB−AuP, respectively. It is interesting to note that the lifetime of the charge shifted state is independent of the excitation wavelength, which implies that the lifetime does not depend on whether the precursor state is ^{1}ZnP or ^{3}AuP. As the total spin is conserved through the ET/HT process, this result shows that there is no difference between a charge shifted state with a (formally) initial total triplet or singlet spin multiplicity. This feature has been observed earlier by Harriman et al.,[43] and it is believed that the strong spin−orbit coupling of AuP efficiently induces a spin flip of the AuP-centered electron to rapidly change the formal total spin to a singlet.

Intrinsic Deactivation of ^{3}AuP at 80 K. The results from nanosecond transient absorption and SPC measurements at 80 K clearly show that the decay of ^{3}AuP cannot be described by including less than three exponentials. It not very likely that the short lifetime could be ascribed to the deactivation of the AuP singlet excited state for several reasons. First, the lifetime of the singlet excited state at room temperature is 240 fs[44] and would need to experience a lengthening of at least 5 orders of magnitude in going from room temperature to 80 K. Second, the three states, corresponding to the three different lifetimes, have the same emission and transient absorption spectra (not shown) which show that they are isoenergetic. Therefore, we assume that the deactivation of the excited triplet manifold involves three different species, arbitrarily called T_{1A}, T_{1B}, and T_{1C}, having lifetimes at 80 K (AuP monomer) of 0.018, 54, and 196 μs, respectively (see Table 2). Although the decrease in the total phosphorescence quantum yield in going from the AuP monomer via the AuP−RB reference to the AuP−RB−ZnP dimers is paralleled by a decrease in the lifetimes, it is the variations in the *initial populations* of the different species that seem to determine the total phosphorescence quantum yield. This is consistent with the fact that the steady-state emission intensities parallel the initial intensities from the time-gated phosphorescent measurements. Although the nature of the different species has still not been established, they could potentially be assigned to three different conformers[48,55−57] or to the three triplet sublevels of T_1, usually referred to as T_x, T_y, and T_z.[58,59] Further work is about to be undertaken in order to examine this matter further.

Quenching of ^{3}AuP at 80 K. On thermodynamic grounds, the quenching of ZnP−BB−^{3}AuP and ZnP−NB−^{3}AuP compared to the corresponding references could in principle have its origin in both hole and triplet energy transfer from ^{3}AuP to ZnP (see Figure 3). TEET would, however, yield ^{3}ZnP, and hence, sensitized ZnP phosphorescence would be expected. Upon closer inspection, the ZnP phosphorescence intensity variation in Figure 5a, as judged by the intensity of the phosphorescence band centered at 719 nm, correlates well with the variation of the corresponding fluorescence intensity through the series of emission spectra. Under the assumption that no other quenching reaction occurs, and with a yield of triplet formation of unity, the efficiency of energy transfer, E_{EET}, can be determined from the following expression

$$E_{\mathrm{EET}} = \left(\frac{I_{\mathrm{DA}}}{I_{\mathrm{A}}} - 1\right)\frac{\epsilon_{\mathrm{A}}}{\epsilon_{\mathrm{D}}} \qquad (4)$$

where I_{DA} and I_{A} are the emission intensities of ZnP in the dimers and in the 1:1 mix, respectively. ϵ_A and ϵ_D are the molar absorption coefficients of ZnP and AuP, respectively. As the ratio ϵ_A/ϵ_D at the excitation wavelength 518 nm is approximately 0.2, an energy transfer efficiency of only 0.10 would give as much as 50% increase in the phosphorescence intensity of ZnP in the dimers compared to the 1:1 mix. This is clearly not observed. In addition, the triplet lifetime of ZnP in the dimers is not decreased compared to the ZnP monomer. Consequently, we can rule out the possibility that sensitization of ^{3}ZnP is canceled by a subsequent quenching reaction. Hence, it is most likely that the major part of the ^{3}AuP quenching at 80 K stems from HT. We are unable to see any sign of quenching of the T_{1A} species in the dimers due to its short lifetime (τ_A), but it is possible to quantify the quenching rate constants from the T_{1B} and the T_{1C} species. Compared to room temperature, the rates of quenching have decreased by 4 orders of magnitude to about 10^3-10^4 s^{-1} (see Tables 1 and 2). Still, there is an alternative explanation consistent with TEET being the origin of the quenching. This, however, implies that only a minor fraction of the AuP triplets are quenched in the dimers—small enough not to appreciably affect the phosphorescence quantum yield of ZnP. This fraction could well be the populations of the T_{1B} and the T_{1C} species, whereas the major part of the triplets decays independently and efficiently to the AuP ground state from T_{1A}. Work is in progress to further elucidate this matter.

Mechanism of the Hole Transfer Process. ET reactions are generally described in terms of either through-space (direct) or through-bond (superexchange) mechanisms. For the direct mechanism to be operative, the donor and acceptor orbitals should overlap, and the overlap decreases exponentially with increasing separation. As the edge-to-edge distance between the donor and acceptor porphyrins in the systems studied is about 19 Å, the overlap between the corresponding orbitals should be negligible. Consequently, we do not expect any significant contribution from the through-space mechanism. The ET/HT reactions studied in this work should therefore be governed by the superexchange mechanism, in which the donor−acceptor electronic coupling is mediated by unoccupied orbitals on the bridging chromophore.[11−13] In this mechanism the electronic coupling for ET/HT, V, and therefore the rate ($k_{ET} \propto V^2$), depend on the donor-bridge and bridge-acceptor couplings, β_{DB} and β_{BA}, respectively, according to

$$V = \frac{\beta_{DB}\beta_{BA}}{\delta E_{DB}} \tag{5}$$

where δE_{DB} is the energy splitting between the initial state and the relevant virtual state involving the bridge. Energetically, the preferred pathway for the superexchange mechanism governing the HT process is via formal oxidation of the bridging chromophore, i.e., electron transfer from the bridge HOMO to AuP to yield ZnP−RB$^{\bullet+}$−AuP$^{\bullet}$ as a virtual state. The energy splittings for this pathway are $\delta E_{DB} = 0.37$ and 0.19 eV for ZnP−BB−AuP and ZnP−NB−AuP, respectively. Hence, according to the superexchange mechanism, the ratio between the rates of HT for ZnP−BB−AuP and ZnP−NB−AuP should equal $(0.37/0.19)^2 = 3.8$. Comparing the observed rate constants for HT at room temperature ($k_A^{AuP,T}$, see Table 1) in the ZnP−BB−AuP and ZnP−NB−AuP dimers gives an experimental value of $6.7 \times 10^8/1.7 \times 10^8 = 3.9$, which is close to the predicted value. It is worth emphasizing that a HT reaction based on a stepwise mechanism, D → B → A, is excluded due to the fact that the room temperature lifetimes of ^{3}AuP in the monomer and the AuP−RB reference substances are equal within experimental uncertainties (cf. Table 1). Hence, no quenching of ^{3}AuP occurs unless the ZnP "hole acceptor" is attached. The most notable result, however, when comparing the relative order of rate constants is that *virtually no HT occurs in the ZnP−OB−AuP dimer regardless of temperature*. This is an observation that has been shown to hold for triplet energy transfer in the corresponding ZnP/H_2P dimer, ZnP−OB−H_2P, as well.[30,31] Recent DFT calculations predict the same result, as the electronic coupling through the OB bridge was found to be essentially zero.[51] It is also encouraging to note that the rates of decay of the charge shifted state, ZnP$^{\bullet+}$−RB−AuP$^{\bullet}$ → ZnP−RP−AuP$^+$, follow the same trend as the HT processes. This is to be expected since the intermediate state in the superexchange governed reaction ZnP−RB$^{\bullet+}$−AuP$^{\bullet}$, is higher in energy for the ZnP−BB−AuP dimer, and consequently the rate should be slower.

As for the results at 80 K, HT was not expected to take place, as studies on a similar ZnP/AuP dimer have shown that HT is efficiently shut off below the glass transition temperature of the solvent.[45] Furthermore, it has been shown for porphyrin-based model systems with quinone or aromatic imide electron acceptors that there is a tendency for the ET/HT driving force to decrease by about 0.8 eV in going from a fluid to a rigid medium, due to restricted ability for solvent reorganization, which destabilizes a charge-separated state.[45,52,53] As the driving force for the HT reaction ZnP−RB−^{3}AuP$^+$ → ZnP$^{\bullet+}$−RB−AuP$^{\bullet}$ in fluid solution is estimated to be 0.6 eV, destabilization of the CTS by 0.8 eV would make the HT reaction endergonic by 0.2 eV. This argument makes the idea of TEET being the origin of quenching at 80 K more attractive. However, the cited studies refer to charge separation reactions rather than charge shift reactions. In addition, the solvent destabilization of charge-separated states in porphyrin−fullerene systems has been shown to be only about 0.4 eV.[54] When both donors and acceptors are porphyrins, the solvent destabilization is likely also smaller than it is in systems with quinone or imide acceptors.

Conclusions

We have investigated the quenching of ^{3}AuP in a series of ZnP−RB−AuP dimers at room temperature and at 80 K. From this study the following has been learned:

1. Long-range hole transfer from ^{3}AuP to ZnP occurs on the nanosecond time scale at room temperature in the dimers connected by fully conjugated bridging chromophores (NB and BB). Conversely, no hole transfer is observed when the bridge conjugation is broken (OB). The relative efficiencies of the hole transfer reactions agree well with what is expected from the superexchange mechanism.
2. Quenching of ^{3}AuP occurs at 80 K in the ZnP−NB−AuP and ZnP−BB−AuP dimers, albeit the rate is drastically decreased compared to room temperature. The origin of the low-temperature quenching is attributed to either hole or triplet energy transfer.
3. The lifetimes of the charge shifted states at room temperature were 30 and 50 ns for ZnP−NB−AuP and ZnP−BB−AuP, respectively.
4. The intrinsic decay of ^{3}AuP is complex at low temperatures, both above and below the glass transition temperature of the solvent. In addition to the two earlier reported lifetimes on the microsecond scale, we have established the presence of a third component with a lifetime on the order of 18 ns at 80 K.
5. The decay dynamics of ^{3}AuP at low temperatures is rather complex, not only due to the triexponential character of the decay. The lifetimes and the initial population of the three different triplet species show a drastic variation caused by minor

changes of the substituents in *meso* positions. It is therefore of the utmost importance to compare the decay characteristics of ^{3}AuP in D−B−A systems with the relevant reference substances.

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