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Photophysical and fluorescence quenching properties of peropyrene in solution

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Abstract

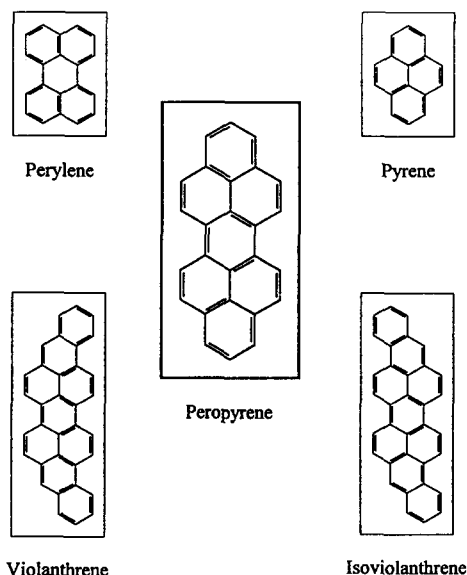
The photophysical properties of peropyrene in toluene and acetonitrile solutions at room temperature were investigated with stationary and time-resolved fluorescence and absorption measurements. Peropyrene is highly fluorescent ($\Phi_F = 0.93$ in toluene) and exhibits several absorption and fluorescence spectroscopic features similar to those of perylene. The absorption spectra of the triplet molecules ($^3PP^*$) and the radical anions ($^2PP^-$) and cations ($^2PP^+$) in acetonitrile were recorded. Photoinduced electron transfer reactions between singlet excited peropyrene ($^1PP^*$) and organic electron acceptors were investigated in acetonitrile. The reaction between $^1PP^*$ and 1,3-dinitrobenzene (DNB) was studied in more detail. The time-resolved detection of $^3PP^*$ and $^2PP^+$ as primary products in the fluorescence quenching process allowed the elucidation of the deactivation of the solvent-separated radical ion pair (SSRIP) $^1(^2PP^+ \cdots ^2DNB^-)$. The rate constants for the spin-allowed and the spin-forbidden charge recombination (CR) reactions were determined to be $k_{CR}^G = (4 \pm 2) \times 10^{10} s^{-1}$ and $k_{CR}^T = (6 \pm 3) \times 10^8 s^{-1}$. Together with the results from our previous studies of intermolecular electron transfer reactions involving perylene and perylene dyes, these rate constants and their dependences on the corresponding free energy changes are discussed within the framework of non-adiabatic electron transfer theory.

Keywords: Peropyrene; Fluorescence quenching; Electron transfer

1. Introduction

The elucidation of the structures and spectroscopic properties of polycyclic aromatic hydrocarbons (PAHs) has traditionally been of central importance in photophysical research. Recently, the properties of PAH molecules are attracting considerable interest owing to promising possible applications in material sciences but also because some members of this class of compounds exhibit carcinogenic activities. Peropyrene is an intriguing compound from the structural point of view since the molecule can either be regarded as containing a central perylene or a peripheral pyrene chromophore and might thus be considered as a dibenzoperylene or, alternatively, as a benzo derivative of pyrene (Scheme 1). Historically, peropyrene was first synthesized by Clar [1] in 1943 for comparison with the then better-known violanthrene and isoviolanthrene dyes.

Following the early characterization by Clar and coworkers [1,2], electrochemical [3], fluorescence quenching [4–6], photoconductive [7], carcinogenic [8] and topographical



Scheme 1.

[9] properties of peropyrene have been studied. Non-planarity effects in peropyrene and some of its benzo derivatives have been investigated [10–12]. However, no systematic

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photophysical study of peropyrene seems to be available at present. In continuation of our spectroscopic studies of larger PAH molecules (e.g. perylene and perylene derivatives [13–18], periflanthene and benzoperiflanthene [19]) we have therefore investigated the photophysical properties of peropyrene (PP) in its ground state (^1PP), lowest excited singlet state ($^1\text{PP}^*$) and lowest excited triplet state ($^3\text{PP}^*$) with stationary and time-resolved absorption and fluorescence spectroscopy. In addition, the present paper also includes a spectroscopic characterization of the radical anionic species ($^2\text{PP}^-$) and cationic species ($^2\text{PP}^+$) and the discussion of fluorescence quenching process in acetonitrile.

2. Experimental details

Peropyrene was obtained commercially from Dr. W. Schmidt (Institute of PAH Research, Greifenberg, Germany). Upon short-wavelength excitation ($\lambda_{\text{exc}} \leq 375$ nm) a small fluorescence signal at around 425 nm was detected, indicating the presence of impurities. Several attempts to purify the peropyrene by recrystallization and high performance liquid chromatography did not significantly improve the situation. With $\lambda_{\text{exc}} \geq 375$ nm the peropyrene fluorescence spectrum was independent of excitation wavelengths and for emission wavelengths $\lambda_{\text{em}} \geq 440$ nm the fluorescence excitation and absorption spectra were identical. Using long-wavelength excitation throughout our work we found no evidence for any adverse effect of the impurities on the results obtained.

The other substances used for sensitization, as reference compounds or as quencher molecules, were purified by recrystallization, sublimation or distillation, if necessary. The solvents toluene and acetonitrile (Aldrich) were of spectroscopic grade and were used without further purification. Peropyrene concentrations employed were in the range $(1-10) \times 10^{-6}$ M. All samples were prepared in 1 cm \times 1 cm cuvettes, deoxygenated by bubbling purified nitrogen through the solutions and then sealed off. Measurements were performed at room temperature.

Fluorescence measurements were carried out with a quantum-corrected Perkin-Elmer MPF-44 fluorescence spectrometer and absorption spectra were recorded with a Shimadzu UV-240 spectrometer. The transient absorption spectroscopy was carried out with a laser flash apparatus described elsewhere [14]. For the laser flash experiments an excimer pumped dye laser was used ($\lambda_{\text{exc}} = 380-440$ nm). The fluorescence decay functions were determined by the method of time-correlated single-photon counting. The measurements were performed with an apparatus described before [20] with a nitrogen-filled nanosecond flash lamp (Edinburgh Instruments) as excitation source. Excitation wavelengths used were in the range $\lambda_{\text{exc}} = 380-410$ nm; the measured fluorescence decay functions were of a single-exponential nature in both solvents.

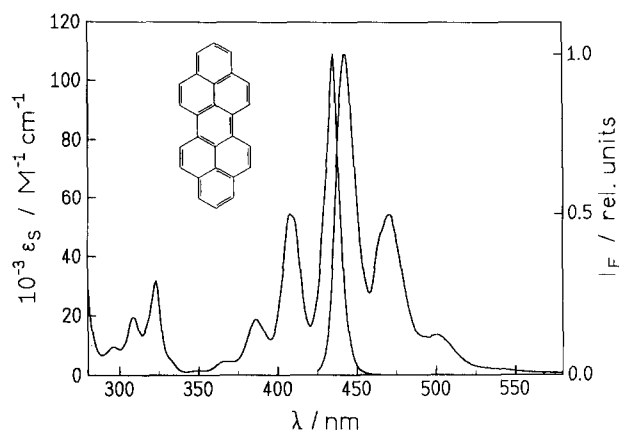


Fig. 1. Absorption and fluorescence spectrum of peropyrene in acetonitrile at room temperature. The fluorescence spectrum was scaled to unity at the short-wavelength maximum.

3. Results and discussion

3.1. Photophysical properties

The singlet absorption (extinction coefficient ϵ_s) and fluorescence spectra of peropyrene in acetonitrile are shown in Fig. 1, and the photophysical properties determined in this work are summarized in Table 1. The absorption and fluorescence spectra exhibit distinct vibrational structures and nearly mirror symmetry. This indicates that the molecule's geometry is quite similar in its ground state S_0 and first excited singlet state S_1 . The high value of ϵ_s at the long-wavelength absorption peak is remarkable. In all solvents investigated, peropyrene was found to be highly fluorescent. The fluorescence quantum yield Φ_F was determined relative to perylene ($\Phi_F = 0.96$ in benzene). Interestingly, the measured fluorescence lifetime τ_F in acetonitrile was found to be almost twice the τ_F in toluene (Table 1).² The strong S_0-S_1 transition observed in both absorption and fluorescence provides clear indication that peropyrene is planar (cf. the significantly less structured spectra of sterically strained peropyrene [11] or perylene [15] derivatives) and possesses a 1L_a -type excited state. Comparing the absorption and fluorescence properties, it can be noted that peropyrene exhibits several spectroscopic features similar to those of perylene.

In Fig. 2 the absorption spectra of peropyrene in the triplet state ($^3\text{PP}^*$; extinction coefficient ϵ_T) and of the cationic ($^2\text{PP}^+$; ϵ_K) and anionic ($^2\text{PP}^-$; relative units) species are shown. The triplet-triplet absorption spectra in acetonitrile and toluene were obtained in sensitization experiments with anthracene ($E(T_1) = 14\,900$ cm $^{-1}$; $\epsilon_T = (42 \pm 4) \times 10^3$ M $^{-1}$

² Whereas in toluene the radiative fluorescence lifetime $\tau_F^0(\text{exp})$ obtained from the τ_F and Φ_F values determined experimentally is in reasonable accordance with the radiative lifetime calculated with the Strickler-Berg [21] formula $\tau_F^0(\text{SB})$, there seems to be a significant deviation in acetonitrile. The ratio $R = \tau_F^0(\text{exp})/\tau_F^0(\text{SB})$ has been taken as measure of the perturbation of the S_1 state (induced for example by mixing-in of other excited states) [22], but the value of $R = 2.0 \pm 0.3$ for peropyrene in acetonitrile is too small to allow definite conclusions ($R = 1.3 \pm 0.2$ in toluene).

cm^{-1} at $\lambda_{\text{max}} = 428.5 \text{ nm}$ [23,24]) as triplet donor. The intersystem crossing quantum yield Φ_{ISC} was measured with the reference excitation technique relative to tetracene in benzene ($E(\text{T}_1) = 10\,250 \text{ cm}^{-1}$; $\epsilon_{\text{T}} = 31.2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda_{\text{max}} = 465 \text{ nm}$ [23,24]; $\Phi_{\text{ISC}} = 0.63$ [25]). It is obvious that the sum $\Phi_{\text{F}} + \Phi_{\text{ISC}}$ (Table 1) for peropyrene is very close to unity, so that internal conversion does not play a significant role in the deactivation from the S_1 state. Use of tetracene as triplet donor did not lead to the formation of $^3\text{PP}^*$ and peropyrene itself did not sensitize the formation of triplet perylene ($E(\text{T}_1) = 12\,400 \text{ cm}^{-1}$ [23]). This locates the T_1 state energy of peropyrene between the T_1 state energies of perylene and tetracene. Hence peropyrene has a large S_1 - T_1 energy gap of about $11\,000 \text{ cm}^{-1}$ as is characteristic for many large PAH molecules. This estimation of the T_1 -state energy is also supported by the experimental triplet lifetime τ_{T} of peropyrene; since the radiationless deactivation from the T_1 state of large PAH molecules depends essentially on the T_1 - S_0 energy gap it is reasonable that the room-temperature triplet lifetimes of peropyrene, tetracene ($\tau_{\text{T}} = 0.6 \text{ ms}$ in benzene [26]) and perylene ($\tau_{\text{T}} = 0.3 \text{ ms}$ in acetonitrile [15]) are very similar.

For the spectroscopic characterization of $^2\text{PP}^+$ in acetonitrile the technique of secondary electron transfer with the 9,10-dicyanoanthracene (DCA)-biphenyl (BP) system was applied [27]. After laser excitation of DCA (concentration, typically 10^{-4} M) the primary electron transfer reaction from BP (oxidation potential $E_{\text{ox}}^{1/2} = 1.93 \text{ V}$ vs. saturated calomel electrode (SCE) [27]; typically 10^{-1} M) produces $^2\text{BP}^+$ with high yields; in the presence of peropyrene (estimated oxidation potential $E_{\text{ox}}^{1/2} = 0.8 \text{ V}$ vs. SCE, cf. next section; typically $(2-10) \times 10^{-5} \text{ M}$), secondary-electron transfer from peropyrene to $^2\text{BP}^+$ leads subsequently to the formation of $^2\text{PP}^+$. These experiments were carried out in air-saturated

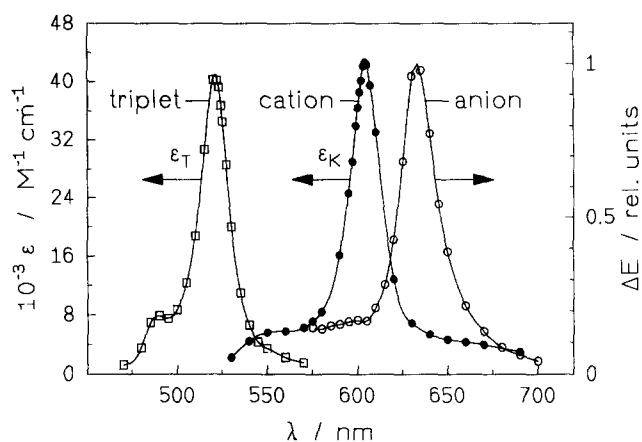


Fig. 2. Absorption spectrum of triplet ($^3\text{PP}^*$; extinction coefficient ϵ_{T}), cationic ($^2\text{PP}^+$; ϵ_{K}) and anionic ($^2\text{PP}^-$; relative units) peropyrene in acetonitrile.

acetonitrile solution. Absolute values of ϵ_{K} for $^2\text{PP}^+$ (cf. Table 1) were determined relative to the *trans*-stilbene cation ($\epsilon_{\text{K}} = 59\,600 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda_{\text{max}} = 508 \text{ nm}$ [28]), generated with the DCA-BP system under identical conditions, and relative to $^2\text{BP}^+$ ($\epsilon_{\text{K}} = 14\,500 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda_{\text{max}} = 670 \text{ nm}$ [27]). The relative ϵ_{K} -determination has the advantage of being independent of the separation efficiency of the DCA-BP ion pair, which has not been determined unequivocally [29].

$^2\text{PP}^-$ was observed after quenching of the peropyrene fluorescence with strong electron-donating species, e.g. *N,N*-dimethylaniline or triphenylamine, in acetonitrile. For these reductive quenching reactions of peropyrene (reduction potential $E_{\text{red}}^{1/2} = -1.69 \text{ V}$ vs. SCE in ethylene glycol monomethyl ether [3]), the photoinduced electron transfer processes and the competing deactivation pathways of the ion pairs were not elucidated in detail (cf. next section). Hence,

Table 1
Photophysical properties of peropyrene in toluene and acetonitrile at room temperature

Parameter (units)	Value in following solvents	
	Toluene	Acetonitrile
$\epsilon_{\text{S}}^{\text{a}}$ ($\text{M}^{-1} \text{ cm}^{-1}$) (λ_{max} (nm))	112000 ± 4000 (442)	109000 ± 6000 (445)
$E_{(\text{S}_1)}^{\text{b}}$ (eV) (wavenumber (10^{-3} cm^{-1}))	2.79 (22.5)	2.83 (22.8)
Φ_{F}	0.93 ± 0.05	0.87 ± 0.05
τ_{F} (ns)	3.0 ± 0.3	5.7 ± 0.3
$\tau_{\text{F}}^{\text{c}}$ (exp) (ns)	3.2 ± 0.4	6.5 ± 0.5
$\tau_{\text{F}}^{\text{d}}$ (SB) (ns)	2.5 ± 0.3	3.3 ± 0.3
$\epsilon_{\text{T}}^{\text{a}}$ ($\text{M}^{-1} \text{ cm}^{-1}$) (λ_{max} (nm))	41000 ± 6000 (522)	41000 ± 6000 (522)
$E_{(\text{T}_1)}^{\text{e}}$ (eV) (wavenumber (10^{-3} cm^{-1}))	≈ 1.4 (≈ 11)	≈ 1.4 (≈ 11)
Φ_{ISC}	0.09 ± 0.02	0.17 ± 0.03
$\tau_{\text{T}}^{\text{f}}$ (ms)	0.6	0.5
$\epsilon_{\text{K}}^{\text{a}}$ ($\text{M}^{-1} \text{ cm}^{-1}$) (λ_{max} (nm))		43000 ± 3000 (604)

^a Extinction coefficients of singlet ground state (ϵ_{S}), triplet (ϵ_{T}) and cationic (ϵ_{K}) peropyrene at the wavelengths given in parentheses.

^b Energies of the S_1 state determined from average wavenumbers of the normalized peaks of the first absorption and emission maxima.

^c Radiative fluorescence lifetimes calculated from the experimental values of τ_{F} and Φ_{F} .

^d Radiative fluorescence lifetimes calculated with the Strickler-Berg formula.

^e Estimated energy of the T_1 state (cf. text).

^f These triplet lifetimes may be affected by impurity quenching.

Table 2
Bimolecular rate constants of peropyrene fluorescence quenching in acetonitrile at room temperature

Number in Fig. 3	Quencher molecule	$E_{\text{red}}^{1/2}$ (V vs. SCE) ^a	ΔG_{CS}^b (eV)	$k_q^{\text{F}c}$ ($\text{M}^{-1} \text{s}^{-1}$)
1	DNB	-0.89	-1.14	2.4×10^{10}
2	Nitrobenzene	-1.14	-0.89	2.8×10^{10}
3	9-Cyanoanthracene	-1.43	-0.60	2.9×10^{10}
4	1-Bromonaphthalene	-2.17	+0.14	3.1×10^8
5	Bromobenzene	-2.32 ^d	+0.29	4.5×10^7

^a Half-wave reduction potential in acetonitrile.

^b Standard free-energy change for CS as calculated from the Weller equation (without work term) for oxidative fluorescence quenching. Reductive fluorescence quenching is energetically unfavourable in all cases.

^c Obtained with stationary measurements from integrated fluorescence spectra; estimated uncertainties of k_q^{F} are about $\pm 10\%$ for $k_q^{\text{F}} \geq 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and about $\pm 30\%$ for $k_q^{\text{F}} \approx 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

^d From [35].

only the relative absorption spectrum of ${}^2\text{PP}^-$ can be presented (Fig. 2).

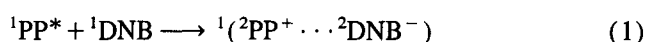
3.2. Fluorescence quenching and charge recombination processes in acetonitrile

The quenching of ${}^1\text{PP}^*$ fluorescence by five organic quencher molecules in their singlet ground states was investigated using stationary fluorescence and laser flash photolysis measurements in acetonitrile solution. The standard free-energy change ΔG_{CS} for the intermolecular electron transfer leading to a charge separation (CS) process and formation of free radical ions was calculated using the Weller equation. The oxidation potential of peropyrene was estimated from the vertical ionization potential (IP_v) determined experimentally according to the linear relationship proposed by Pysh and Yang [30]: $E_{1/2}^{\text{ox}} = a + b \times \text{IP}_v$. In practice, a combination of the experimental data available for perylene and pyrene as reference compounds (R) was considered to yield the most reliable result: $E_{1/2}^{\text{ox}}(\text{peropyrene}) = E_{1/2}^{\text{ox}}(\text{R}) + b[\text{IP}_v(\text{peropyrene}) - \text{IP}_v(\text{R})]$. With $E_{1/2}^{\text{ox}} = 1.0 \text{ V}$ vs. SCE and 1.3 V vs. SCE for perylene and pyrene respectively [18,31] (acetonitrile), $\text{IP}_v = 7.00 \text{ eV}$, 7.41 eV and 6.77 eV for perylene, pyrene and peropyrene respectively [32], $b = (0.80 \pm 0.15)$ [30], $E_{1/2}^{\text{ox}}(\text{peropyrene}) = 0.8 \text{ V}$ vs. SCE (acetonitrile; estimated uncertainty, about $\pm 0.1 \text{ V}$) was obtained. This value is consistent with other estimations from molecular-orbital-based correlations between oxidation potentials and excited-state energies [33] or Hückel coefficients [34]. Experimental fluorescence quenching rate constants k_q^{F} (Table 2) were obtained using the modified Stern-Volmer equation introduced by Weller [36]. Diffusion coefficients were estimated as described previously [18,37] and the values employed were $D = 1.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $2.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for peropyrene and the quencher molecules in acetonitrile.

The $\log k_q^{\text{F}}$ values of the oxidative peropyrene fluorescence quenching are presented, together with results from the flu-

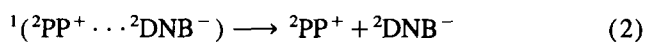
orescence quenching of perylene [13] and 1,7-diazaperylene [18], as function of ΔG_{CS} in Fig. 3 (Rehm–Weller plot). The curve in Fig. 3 was calculated using the kinetic scheme (steady-state conditions) and the parameters reported originally by Rehm and Weller [38] for the fluorescence quenching of aromatic molecules in acetonitrile. While the k_q^{F} values measured tend to be somewhat larger than predicted by the Rehm–Weller parameters, there is obviously good qualitative agreement between the calculated curve and the experimental data. This underlines that the empirical Rehm–Weller treatment provides an adequate overall description of the investigated peropyrene fluorescence quenching processes in acetonitrile.

It is well known that intermolecular electron transfer processes in polar solvents involve solvent-separated radical ion pairs (SSRIPs) as intermediates. As an example, the oxidative quenching of peropyrene fluorescence by 1,3-dinitrobenzene (DNB) as described by



(standard free-energy change $\Delta G_{\text{CS}} = -1.14 \text{ eV}$)

was investigated in more detail. The deactivation of the initially formed singlet SSRIP, ${}^1({}^2\text{PP}^+ \dots {}^2\text{DNB}^-)$ (Eq. (1)), is governed by the separation into free ions, given by



(rate constant k_{sep})

and the spin-allowed and spin-forbidden charge recombination (CR) reactions to the peropyrene ground state, given by



(rate constant k_{CR}^{G} ; standard free-energy change $\Delta G_{\text{CR}}^{\text{G}} = -1.69 \text{ eV}$)

and to the triplet state, given by

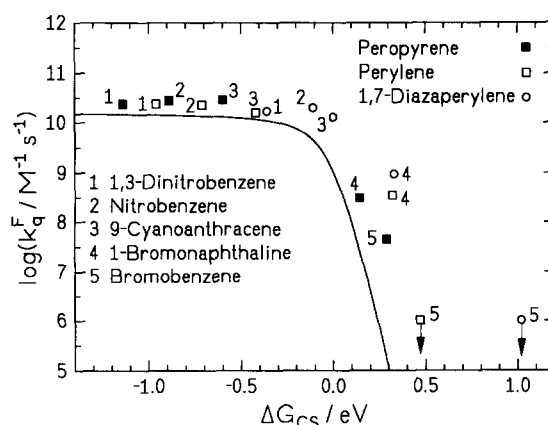


Fig. 3. Logarithmic rate constants k_q^{F} of peropyrene fluorescence quenching as a function of free-energy change ΔG_{CS} for charge separation in acetonitrile. Also shown are results for fluorescence quenching of perylene [13] and 1,7-diazaperylene [18]. The curve was calculated with the original parameters given by Rehm and Weller [38].

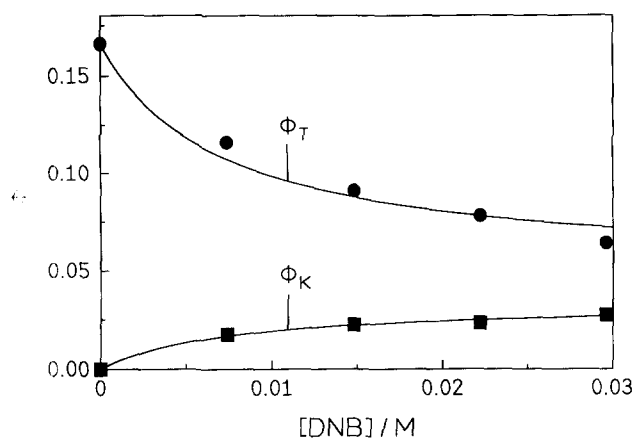


Fig. 4. Dependences of triplet peropyrene formation efficiency Φ_T and cationic peropyrene formation efficiency Φ_K on the DNB concentration in acetonitrile. The curves were obtained from non-linear fitting of the corresponding Stern–Volmer expressions (Eqs. (5) and (6)).

(rate constant k_{CR}^T ; standard free-energy change $\Delta G_{CR}^T \approx -0.3$ eV).

The experimental rate constants k_q^K and k_q^T for the formations of ${}^2PP^+$ and ${}^3PP^*$ (formation efficiencies Φ_K and Φ_T) as primary products in the fluorescence quenching were determined as a function of the DNB concentration [DNB]. Owing to the low extinction coefficient of ${}^2DNB^-$ in the spectral region of interest ($\epsilon_A \approx 3000$ M $^{-1}$ cm $^{-1}$ at $\lambda_{max} = 487$ nm [39]), no absorbance signal from the quencher radical anion was observed. The results presented in Fig. 4 show the enhancement of ${}^2PP^+$ formation with increasing DNB concentration, whereas the triplet yield Φ_T is reduced. The latter effect is because, with increasing DNB concentration, the increasing triplet formation from the SSRIP (Eq. (4)) is overcompensated by the reduction in the lifetime of the peropyrene S_1 state and, hence, by the reduction in the triplet formation therefrom. In order to obtain the rate constants k_{CR}^G and k_{CR}^T a Stern–Volmer type analysis with non-linear fitting of the functions Φ_K , $\Phi_T = f([DNB])$, obtained from the kinetic fluorescence quenching scheme under steady-state conditions, can be performed [14]:

$$\Phi_T = \frac{\Phi_{ISC} + k_q^T \tau_F [DNB]}{1 + k_q^F \tau_F [DNB]} \quad (5)$$

$$\Phi_K = \frac{k_q^K \tau_F [DNB]}{1 + k_q^F \tau_F [DNB]} \quad (6)$$

(with $k_q^T/k_q^F = k_{CR}^T/k_S$, $k_q^K/k_q^F = k_{sep}/k_S$, $k_S = k_{sep} + k_{CR}^G + k_{CR}^T$). Alternatively, for the data evaluation, the following linear relationship between Φ_T/Φ_K and the inverse DNB concentration was also used here:

$$\frac{\Phi_T}{\Phi_K} = \Phi_{ISC} \frac{k_S}{k_{sep} k_q^F \tau_F [DNB]} + \frac{k_{CR}^T}{k_{sep}} \quad (7)$$

This analysis has the advantage that it requires only the ratio Φ_T/Φ_K , which can be determined from the triplet and cation absorbance signals measured in one sample at 522 and 604

nm (cf. Fig. 2) and the known extinction coefficients (Table 1), i.e. the absolute determination of the formation efficiencies by the reference excitation method is not necessary.

The evaluation of data according to Eq. (7), shown in Fig. 5, yielded k_{CR}^T/k_{sep} directly from the intercept and then, with known values of Φ_{ISC} , τ_F and k_q^F , from the slope, k_S/k_{sep} and thus k_{CR}^G/k_{sep} was obtained. Taking the rate constant of separation into free ions to be $k_{sep} = 1 \times 10^9$ s $^{-1}$ [14], we obtained for the fluorescence quenching of peropyrene by DNB in acetonitrile: $k_{CR}^G = (4 \pm 2) \times 10^{10}$ s $^{-1}$ and $k_{CR}^T = (6 \pm 3) \times 10^8$ s $^{-1}$. These values can be compared with our investigation of the fluorescence quenching of perylene and perylene dyes and the quantitative interpretation of the dependence of k_{CR} on ΔG_{CR} in the framework of non-adiabatic electron transfer reactions [14,17]. As predicted by the Marcus theory, plots of $\log k_{CR}^G$ vs. ΔG_{CR}^G exhibit a characteristic bell-shaped behaviour determined essentially by the reorganization energy λ and the electronic matrix coupling element V as crucial electron transfer parameters. Comparison with our earlier studies reveals that the value of $k_{CR}^G = (4 \pm 2) \times 10^{10}$ s $^{-1}$ at $\Delta G_{CR}^G = -1.69$ eV determined here from the peropyrene fluorescence quenching is in good accordance with the electron transfer parameters determined previously ($\lambda \approx 1.5$ eV; $V \approx (2-3) \times 10^{-3}$ eV) [14,17]. Hence, if we tentatively assume that the reorganization energies of electron transfer reactions involving peropyrene and the perylenes in acetonitrile are similar, it follows that the spin-allowed CR reaction from the SSRIP (${}^1({}^2PP^+ \dots {}^2DNB^-)$) to the peropyrene ground state is located slightly in the Marcus inverted regime.

While the investigation of spin-forbidden CR reactions has attracted some attention, a possible influence of ΔG_{CR}^T on k_{CR}^T has not yet clearly been established for the deactivation of singlet ion pairs. This has to do with the fact that the singlet SSRIP deactivation formally described by Eq. (4) is considered to be composed of two processes: spin evolution leading to the formation of triplet ion pairs (${}^1({}^2PP^+ \dots {}^2DNB^-) \rightarrow {}^3({}^2PP^+ \dots {}^2DNB^-)$) followed by

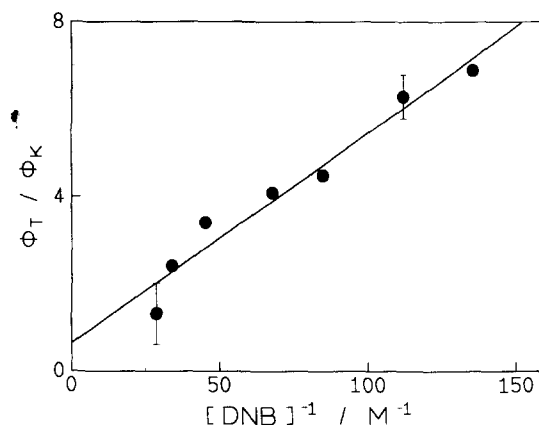


Fig. 5. Dependence of the ratio Φ_T/Φ_K of triplet to cationic peropyrene formation efficiencies on the inverse DNB concentration in acetonitrile. The linear regression according to Eq. (7) gave $a = 0.6 \pm 0.3$ as intercept and $m = 0.05 \pm 0.01$ M as slope.

the spin-allowed triplet formation ($^3(^2\text{PP}^+ \dots ^2\text{DNB}^-) \rightarrow ^3\text{PP}^* + ^1\text{DNB}$). In our previous work we found preliminary experimental evidence that the overall deactivation rate constant was independent of $\Delta G_{\text{CR}}^{\text{T}}$ ($k_{\text{CR}}^{\text{T}} = (3.5 \pm 2.5) \times 10^8 \text{ s}^{-1}$, in the absence of heavy-atom perturbation) [14]. Such a behaviour is to be expected if the spin evolution is the rate-determining step in the deactivation. The k_{CR}^{T} value determined in the present work is consistent with such an interpretation which, however, can only be preliminary at present.

4. Conclusions

In this work, the photophysical and fluorescence quenching properties of peropyrene were investigated. In acetonitrile, the bimolecular rate constants of fluorescence quenching can adequately be described with Rehm–Weller plots. Taking DNB as an exemplary quencher molecule, we found that the electron transfer parameters (matrix coupling element V and reorganization energy λ) of the charge recombination reactions are in accordance with data obtained from intermolecular electron transfer reactions of perylene and perylene dyes.

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