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Singlet-energy transfer in quadruple hydrogen-bonded oligo(*p*-phenylenevinylene)perylene-diimide dyads

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The photophysical properties of a supramolecular donor–acceptor dyad consisting of an oligo(*p*-phenylenevinylene) unit and a perylene-diimide unit are described. The dyad is created by functionalising the two chromophores with quadruple hydrogen bonding 2-ureido-4[1*H*]-pyrimidinone units, which provide a high association constant ($K \approx 10^8$ M^{-1} in toluene). This feature enabled us to study the time-resolved photoinduced singlet-energy transfer reaction between the two chromophores in dilute solution with transient pump-probe spectroscopy. This energy transfer occurs with a time constant of 5.1 ps.

Introduction

Non-covalent interactions between organic molecules are ubiquitous in nature and serve to assemble, position and organize extended architectures that fulfil complex functions. The photosynthetic reaction centre is an intriguing example of such a structural design. Here, photoinduced energy and electron transfer reactions between carefully aligned molecular arrays of photo- and redox-active components work in concert to convert and store solar energy.[1] Because hydrogen bonding is often a key element in structuring the natural systems, the study of photoinduced energy and electron transfer reactions between donors and acceptors assembled *via* hydrogen bonding interactions has attracted considerable interest in recent years.[2,3] Hydrogen bonds, however, represent a fairly weak interaction and generally result in low association constants. Consequently, only a small fraction of the donors and acceptors remain associated, while the remaining molecules are free to diffuse in solution, especially at low concentrations. This problem can be alleviated by using multiple hydrogen-bonded arrays designed to gain strength and directionality.[4] The 2-ureido-4[1*H*]-pyrimidinone (UP) quadruple hydrogen-bonding unit, for example, dimerises in a self-complementary array of four cooperative hydrogen bonds and provides association constants in excess of 10^7 M^{-1} in organic solvents.[5] Utilizing these high association constants it is possible to construct supramolecular polymers.[6] Recently the UP unit has been utilized to create hydrogen-bonded donor–acceptor dyads[7] based on photo- and redox-active oligo(*p*-phenylenevinylene) (OPV)[8] and [60]fullerene (C_{60})[9] derivatives. Photovoltaic cells based on supramolecular OPV polymers have demonstrated that the hydrogen bonds of the UP unit can be incorporated into working opto-electronic devices.[10]

Perylene-diimides have been extensively studied as organic semiconductors in electronic and optical applications such as field-effect transistors,[11] fluorescent solar collectors,[12] electrophotographic devices,[13] photovoltaic devices,[14] dye lasers,[15] and molecular switches.[16] These perylene-diimides have outstanding chemical, thermal and photochemical stability.[17] We recently reported on photoinduced electron transfer in liquid crystalline oligo(*p*-phenylenevinylene)–perylene-diimide–oligo(*p*-phenylenevinylene) (OPV-PERY-OPV) arrays and in π-stacks of triple hydrogen-bonded OPV–PERY–OPV trimers.[18,19] Here we extend these studies and describe the synthesis of a perylene-diimide with the donor–donor–acceptor–acceptor (DDAA) four-point hydrogen bonding motif UP-unit (PERY-UP) and study its photophysical properties in hetero-assemblies with OPV-UP (Fig. 1) using fluorescence spectroscopy and femtosecond pump-probe spectroscopy. The high association constant of the heterodimer allowed us to time resolve the singlet-energy transfer reaction in this supramolecular system by femtosecond pump-probe spectroscopy.

Results and discussion

Synthesis

The preparation of OPV-UP has been described previously.[8] The synthetic route to PERY-UP is shown in Scheme 1. *N,N′*-bis-(1-ethylpropyl)perylene-3,4:9,10-tetracarboxylic diimide **1**[20] was partially hydrolysed with potassium hydroxide in *tert*-butanol to the anhydride imide **2**.[21,22] Anhydride imide **2** was subsequently reacted with 2,5-di-*tert*-butylbenzene-1,4-diamine[23] in the presence of zinc acetate in molten imidazole to afford the asymmetric perylene-diimide **3**. PERY-UP was obtained by reaction of **3** with carboxamide **4**[24] in chloroform.

Keto–enol equilibrium

The UP-unit of OPV-UP and PERY-UP can exist in two different tautomeric forms.[25] Apart from the pyrimidinone tautomer (keto) with a DDAA motif, the pyrimidinol tautomer (enol) exists. Both keto and enol forms are self-complementary with DDAA and DADA motifs, respectively, but cannot associate with each other. The keto–enol equilibrium depends on the polarity of the solvent and the nature of the substituent on the isocytosine moiety. The keto tautomer is known to have a higher dimerisation constant ($K = 6 \times 10^7$ M^{-1} in water-saturated chloroform; 6×10^8 M^{-1} in toluene) than the enol tautomer ($K = {\sim}10^5$ M^{-1} in chloroform),[25,26] as a result of more favourable secondary interactions.[27,28]

^{1}H NMR spectroscopy has been used to determine the relative amounts of the keto and enol tautomers of PERY-UP in different solvents by comparing the integrated signals of the N–H protons. For PERY-UP the amount of keto is 80% in $CDCl_3$, while it decreases to 50% in toluene-d_8. These ratios are >99% ($CDCl_3$) and 90% (toluene-d_8) for OPV-UP.[7] As a consequence, not all PERY-UP molecules can bind to OPV-UP molecules and we assume that in a 1 : 1 mixture of PERY-UP and OPV-UP, both homodimers and the heterodimer are simultaneously present.

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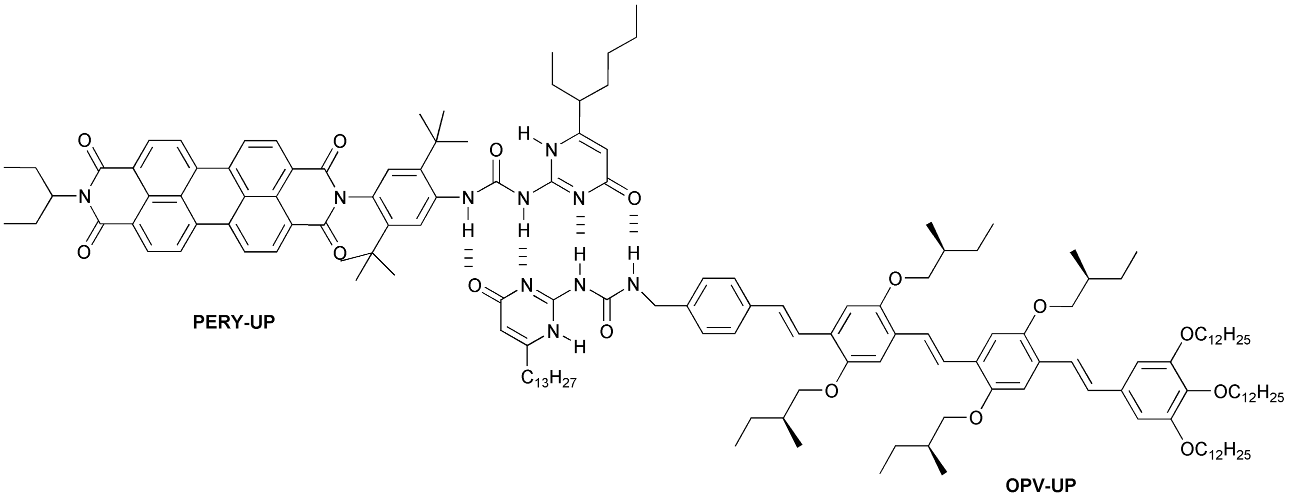
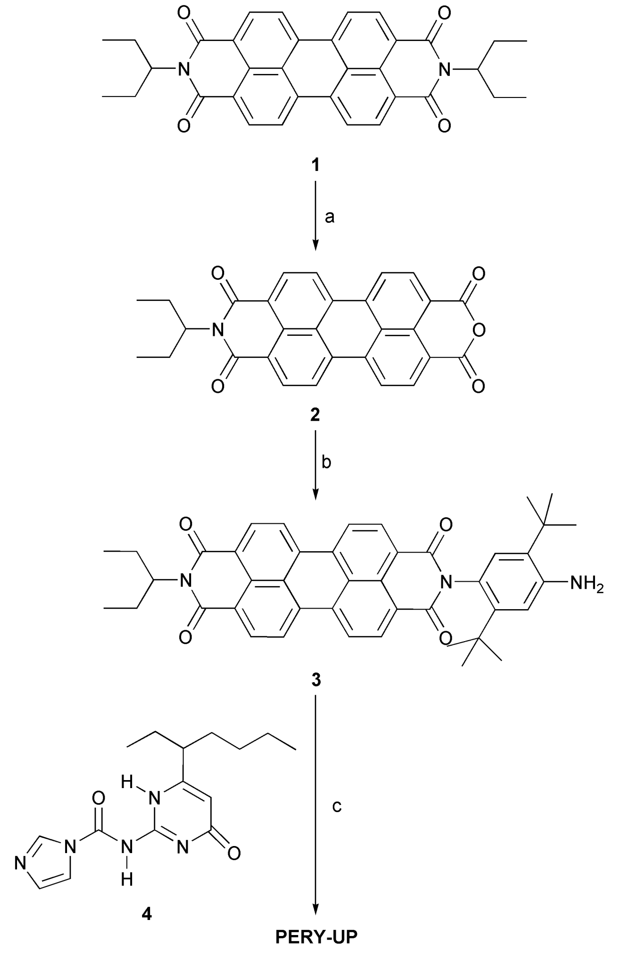


Fig. 1 Heterodimer of PERY-UP and OPV-UP bound by quadruple hydrogen bonds.



Scheme 1 Synthesis of PERY-UP. a) KOH, *tert*-butanol; b) 2,5-di-*tert*-butylbenzene-1,4-diamine, imidazole, $Zn(OAc)_2$, 160 °C, 3.5 h; c) $CHCl_3$, reflux, 18 h.

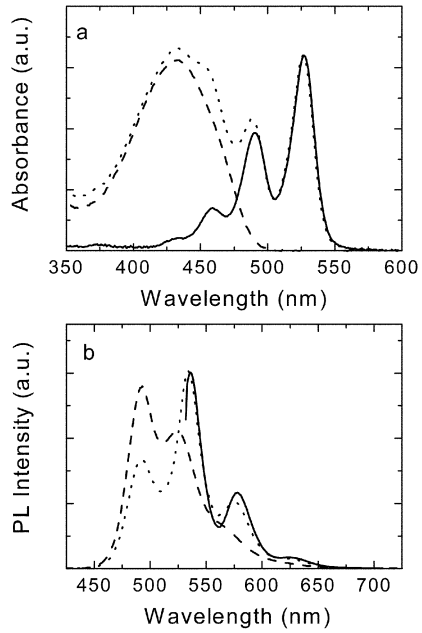


Fig. 2 Absorption (a) and emission (b) spectra of PERY-UP (——), OPV-UP (- - -) and a 1 : 1 mixture of PERY-UP and OPV-UP (· · ·) in toluene solution. The excitation wavelength is 527 nm for PERY-UP and 410 nm for OPV-UP and the mixture.

Optical properties

The absorption and photoluminescence spectra of PERY-UP, OPV-UP and a 1 : 1 mixture of the two compounds in toluene are shown in Fig. 2. The characteristic absorption peaks of the perylene-diimide are at 459 nm, 490 nm and 527 nm for PERY-UP. The absorption spectrum of OPV-UP is not structured and maximizes at 432 nm. Both compounds fluoresce in toluene solution with very high quantum yields.[7,20] The fluorescence spectra reveal that the singlet-excited state (S_1) of OPV-UP ($E(S_1)$ = 2.52 eV) is higher in energy than the singlet-excited state of PERY-UP ($E(S_1)$ = 2.32 eV). Fluorescence lifetimes (τ) for OPV-UP and PERY-UP are 1.23 and 3.61 ns, respectively, as determined from time-correlated single photon counting (TCSPC) with excitation at 400 nm. The absorption spectrum of the mixture closely resembles the superposition of the spectra of the two compounds and gives no evidence of a significant electronic interaction. In dichloromethane, the oxidation potential of OPV-UP is E_{ox} = 0.71 V *vs.* SCE and the first reduction potential of PERY-UP is E_{red} = −0.61 V *vs.* SCE.

Fluorescence quenching

Fluorescence quenching has been used to study the steady-state photophysics of OPV-UP–PERY-UP heterodimers. As a result of the ordering of the singlet states and the difference between oxidation and reduction potentials, the singlet-excited state of OPV-UP can act as a donor towards PERY-UP in both photoinduced energy and photoinduced electron transfer reactions. Both processes are expected to quench the OPV-UP fluorescence, when their rate is competitive with the intrinsic decay of OPV-UP.

The OPV-UP fluorescence quenching was studied by adding a mixture of 2 × 10^{-5} M PERY-UP and 10^{-6} M OPV-UP in small aliquots to a solution of 10^{-6} M OPV-UP in toluene. Almost selective excitation of OPV-UP in the mixtures was achieved by irradiation at 410 nm and the fluorescence signal at 493 nm (OPV-UP fluorescence only) was followed as a function of the PERY-UP concentration in the mixture. A significant quenching of the OPV-UP fluorescence was observed. The quenching factor Q, *i.e.* the ratio of initial OPV-UP fluorescence (I_0) and that of the mixture (I) is plotted in Fig. 3 after correction for absorption by PERY-UP.[29] The Stern–Volmer constant, defined as $K_{SV} = (Q\text{-}1)/[\text{PERY-UP}]$, amounts to $K_{SV} = 5.9 \times 10^5$ M^{-1} for concentrations of PERY-UP up to 1.13 × 10^{-6} M. Two control experiments were performed, in each experiment one of the two chromophores lacks the hydrogen bonding UP-group. The first control used **1** instead of PERY-UP together with OPV-UP and in the second experiment PERY-UP was mixed with a methyl end-capped oligo-(*p*-phenylenevinylene) with four phenyl rings (OPV4)[30] instead of OPV-UP. In both cases no fluorescence quenching was observed (Fig. 3). This indicates that dynamic or collisional quenching is not important at these low concentrations and that the quenching can unambiguously be ascribed to the formation of OPV-UP–PERY-UP heterodimers.

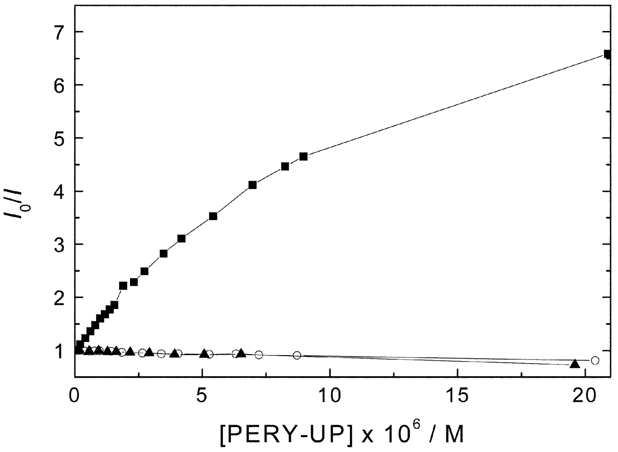


Fig. 3 Stern–Volmer plot of OPV fluorescence quenching by PERY derivatives in toluene solution. Curves are shown for OPV-UP + PERY-UP (■); OPV-UP + **1** (○); and OPV4 + PERY-UP (▲). The OPV chromophore concentration is 10^{-6} M in each experiment and the excitation wavelength 410 nm. The detection wavelength is 493 nm for OPV-UP and 500 nm for OPV4.

The origin of the OPV fluorescence quenching in the OPV-UP–PERY-UP heterodimers can be inferred from the photoluminescence spectrum (Fig. 2b) of the mixture. When the 1 : 1 mixture is excited at 410 nm, the fluorescence of the PERY-UP unit dominates the photoluminescence spectrum even though the absorption at 410 nm of this chromophore is negligible. Hence the OPV-UP unit acts as a sensitiser for the PERY-UP fluorescence. This indicates that a singlet-energy transfer, rather than electron transfer, occurs in the heterodimer in toluene in which the photoexcited OPV-UP S_1 state evolves to PERY-UP S_1.

Transient photoinduced absorption

Sub-picosecond transient pump-probe spectroscopy (150 fs pulses) was performed at room temperature on OPV-UP–PERY-UP solutions to assess the temporal evolution of the singlet-energy transfer on short timescales. Upon preferential photoexcitation of the OPV-UP moiety at 450 nm in a mixture of 4 × 10^{-5} M OPV-UP and 2 × 10^{-4} M PERY-UP in toluene, a negative differential transmission was observed by probing at 900 nm (Fig. 4). At 900 nm the $S_n \longleftarrow S_1$ photoinduced absorption of the OPV chromophore is present.[31] The dynamics in the low picosecond time range (Fig. 4, ○) show a rapid decay which can be fitted to a mono-exponential decay with a time constant of 5.1 ps, *i.e.* a rate of $k = 1.9 \times 10^{11}$ s^{-1}. On longer time scales (Fig. 4, ●) a much slower decay is visible with a mono-exponential time constant of 1.1 ns. The two different decay times account for the fact that under these conditions both OPV-UP–PERY-UP heterodimers and OPV-UP–OPV-UP homodimers are present. It is important to note that a control experiment confirmed that the $S_n \longleftarrow S_1$ photoinduced absorption of the PERY chromophore has only a small (~10%) contribution to the photoinduced absorption at 900 nm. The fast (5.1 ps) decay is attributed to the singlet-energy transfer reaction from OPV-UP(S_1) to PERY-UP in the heterodimer, while the slow (1.1 ns) decay represents the intrinsic relaxation of OPV-UP(S_1) in the homodimer. The lifetime of the latter process is close to the photoluminescence lifetime of 1.23 ns of OPV-UP homodimers, determined by TCSPC.[7]

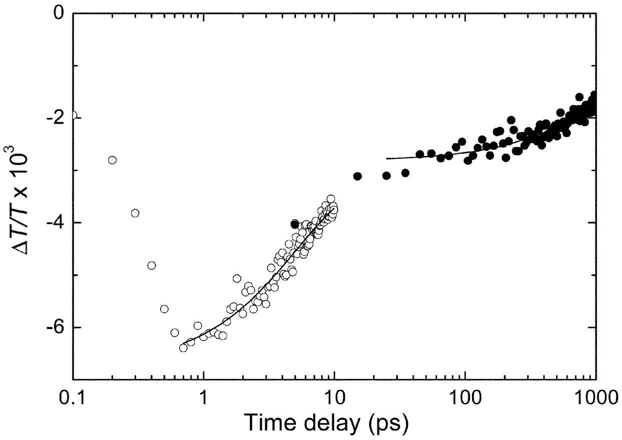


Fig. 4 Differential transmission dynamics of the OPV ($S_n \longleftarrow S_1$) absorption at 900 nm as a function of the pump-probe time delay after photoexcitation at 450 nm. The concentration PERY-UP is 2 × 10^{-4} M and the concentration OPV-UP is 4 × 10^{-5} M in toluene. Solid lines are fits to decays with time constants of 5 ps and 1100 ps.

Förster energy transfer

The fluorescence quenching studies provide a lower limit for the rate for singlet-energy transfer *via* the Stern–Volmer constant by:

$$k_{EN} = \frac{Q_{\max} - 1}{\tau} \qquad (1)$$

using the highest quenching observed in the titration experiment, $Q_{\max} = 6.6$, and $\tau = 1.23$ ns, the lower limit for k_{EN} is 4.5 × 10^9 s^{-1}. Of course, $Q_{\max}$ is limited by the presence of OPV-UP homodimers and the highest ratio of PERY-UP : OPV-UP (21.6 : 1) used in the experiment. The actual value, $k_{EN} = 1.9 \times 10^{11}$ s^{-1}, determined from the transient spectroscopy, is over 40 times faster.

The Förster equation[32] can be used to estimate the distance d between the centres of the donor and acceptor chromophores in the energy transfer process.

$$k_{EN} = \frac{1}{\tau}\cdot\frac{9000(\ln 10)\kappa^2\phi}{128\pi^5 N_{av} n^4 d^6} J_F = \frac{1}{\tau}\left(\frac{R_c}{d}\right)^6 \qquad (2)$$

In eqn. (2), the parameters N_{av} and n represent Avogadro's number and the refractive index of the medium, ϕ is the fluorescence quantum yield of the donor in the absence of transfer, R_c the Förster radius and d is the actual centre-to-centre distance of the two chromophores involved in the energy transfer. J_F represents the overlap between the absorption ($\varepsilon(\bar{v})$)

Table 1 Change in free energy for charge separation $\Delta G_{CS}{}^{a}$/eV from OPV(S_1) and PERY(S_1), and solvent reorganization energy λ_s/eV for OPV-UP–PERY-UP heterodimers in different solvents from eqns (5) and (7)

	$\Delta G_{CS}{}^{OPV}$	$\Delta G_{CS}{}^{PERY}$	λ_s
Toluene	−0.47	−0.27	0.07
odcb	−1.28	−1.08	0.79
Benzonitrile	−1.43	−1.23	0.98

[a] $\Delta G_{CS}{}^{OPV}$ uses E_{00} = 2.52 eV; $\Delta G_{CS}{}^{PERY}$ uses E_{00} = 2.32 eV.

of the acceptor (PERY-UP) and the fluorescence ($F(\bar{\nu})$) of the donor (OPV-UP) on an energy scale (cm^{-1}) defined as:

$$J_F = \frac{\int [F(\bar{\nu})\varepsilon(\bar{\nu})/\bar{\nu}^4]d\bar{\nu}}{\int F(\bar{\nu})d\bar{\nu}} \qquad (3)$$

The factor κ is the so-called orientation factor, which incorporates the dependence of the energy transfer rate on the mutual orientation of the transition dipole moments of donor and acceptor chromophores. It can be expressed as:

$$\kappa = \cos(\Theta_{DA}) - \cos(\phi_{DR})\cos(\phi_{AR}) \qquad (4)$$

where Θ_{DA} is the angle between the transition dipole moments of donor and acceptor and ϕ_{DR} (ϕ_{AR}) is the angle between the transition dipole moment of the donor (acceptor) chromophore and the line joining the centres of the two chromophoric units. In calculating values for κ^2, we have assumed that rotation around the bond joining the UP unit and the methylene group connecting the UP and the OPV moieties is possible. For various conformations we find values for κ^2 ranging from 2.5 to 3.5. Using the following numbers for the OPV-UP–PERY-UP combination, $J_F = 1.55 \times 10^{-13}$ cm^6 mol^{-1}, $k_{EN} = 1.9 \times 10^{11}$ s^{-1}, τ = 1.23 ns, ϕ = 0.84,[7] κ^2 = 3, we obtain using eqns. (2) and (3): R_c = 64 Å and d = 26 Å. The latter value is slightly less than the centre-to-centre distance estimated from molecular modelling (~33 Å). The difference can be rationalized by considering that the singlet-excited states delocalise and effectively reduce the centre-to-centre distance. A similar result has been found for energy transfer reactions in covalent OPV4-C_{60} donor–acceptor systems.[31]

Electron transfer

Why does singlet-energy transfer occur from the OPV-UP singlet state rather than electron transfer and is electron transfer possibly subsequent to energy transfer from the singlet-excited state of PERY-UP? To address these questions it is instructive to consider the change in free energy for charge separation using the Weller equation:[33,34]

$$\Delta G_{cs} = e\left(E_{ox}(\mathrm{D}) - E_{red}(\mathrm{A})\right) - E_{00} - \frac{e^2}{4\pi\varepsilon_0\varepsilon_s R_{cc}} - \frac{e^2}{8\pi\varepsilon_0}\left(\frac{1}{r^+}+\frac{1}{r^-}\right)\left(\frac{1}{\varepsilon_{ref}}-\frac{1}{\varepsilon_s}\right) \qquad (5)$$

Table 1 shows that according to eqn. (5) photoinduced electron transfer is energetically possible for the OPV-UP–PERY-UP heterodimer in solvents of varying polarity from either the OPV-UP or the PERY-UP singlet-excited states.

To investigate the possibility for electron transfer in the heterodimer in more detail, the fluorescence signal of PERY-UP at 578 nm was monitored after selective photoexcitation of PERY-UP at 527 nm as a function of an increasing amount of OPV-UP. For this purpose, a solution of 2×10^{-5} M OPV-UP and 10^{-6} M PERY-UP was added in steps to a 10^{-6} M solution of PERY-UP. Irrespective of the polarity of the solvent (toluene, ε = 2.38; *o*-dichlorobenzene (odcb), ε = 9.93; benzonitrile, ε = 25.18) the PERY-UP fluorescence signal remained constant. From this experiment it can be concluded that photoinduced electron transfer does not occur in the heterodimer from the PERY-UP S_1 state.

If electron transfer is absent but thermodynamically feasible, it is likely to be hampered kinetically. The expression for the rate constant for non-adiabatic charge separation:

$$k_{cs} = \left(\frac{4\pi^3}{h^2\lambda k_B T}\right)^{1/2} V^2 \exp\left[\frac{-\Delta G^{\ddagger}_{cs}}{k_B T}\right] \qquad (6)$$

shows that k_{cs} is determined by the coupling (V) between donor and acceptor in the excited state, the reorganization energy λ and the barrier for charge separation ($\Delta G^{\ddagger}_{cs} = (\Delta G_{cs} + \lambda)^2/4\lambda$). The reorganization energy is the sum of internal (λ_i) and solvent (λ_s) contributions. The latter can be estimated from:[35]

$$\lambda_s = \frac{e^2}{4\pi\varepsilon_0}\left[\frac{1}{2}\left(\frac{1}{r^+}+\frac{1}{r^-}\right) - \frac{1}{R_{cc}}\right]\left(\frac{1}{n^2}-\frac{1}{\varepsilon_s}\right) \qquad (7)$$

and the results for OPV-UP–PERY-UP are collected in Table 1. The internal reorganization energy λ_i is probably not very high for these extended conjugated systems and is estimated to be in the range of 0.2 to 0.5 eV. Within these limits the barrier $\Delta G^{\ddagger}_{cs}$ for charge separation from PERY-UP(S_1) remains less than 0.01 eV in odcb and benzonitrile, and is only slightly higher in toluene (<0.04 eV). The absence of electron transfer in each of these solvents is therefore ascribed to a very weak electronic coupling V of donor and acceptor in the excited state, rather than a high barrier. V is known to be exponentially dependent on the distance between donor and acceptor. Molecular modelling and the value derived from the Förster equation, indicate an appreciable distance between OPV-UP and PERY-UP units in the heterodimer, causing a low V. In agreement with this proposition, a photoinduced electron transfer reaction does occur between OPV and PERY chromophores in systems were the two redox-active chromophores are at a much shorter distance.[18,19]

Conclusion

Photoluminescence studies reveal that a singlet-energy transfer reaction occurs in quadruple hydrogen-bonded OPV-UP–PERY-UP heterodimers (Fig. 1) after excitation of the OPV chromophore. As a result of the high association constant of the quadruple hydrogen bond, significant amounts of heterodimers and homodimers are present, even in dilute solutions. This feature enabled us to follow the temporal evolution of the singlet-energy transfer reaction using sub-picosecond transient absorption spectroscopy in the heterodimers on short timescales. The time constant of 5.1 ps was obtained for this reaction is in fair agreement with Förster theory. The singlet-excited in OPV-UP homodimers, is much longer lived and decays with a time constant of 1.1 ns. Although exergonic, electron transfer does not occur after photoexcitation as a result of a too weak electronic coupling between OPV and PERY chromophores in the excited state. To achieve photoinduced electron transfer in quadruple hydrogen-bonded systems based on the UP unit a judicious design of the relative positioning of donor and acceptor will be required.

Experimental

General methods

^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature on a Varian Gemini 300 MHz or a Varian Mercury 400

MHz spectrometer. Chemical shifts are given in ppm (δ) relative to tetramethylsilane. Matrix assisted laser desorption ionisation time of flight (MALDI-TOF) mass spectrometry was conducted on a Perseptive Biosystems Voyager DE-Pro MALDI-TOF mass spectrometer. UV/Vis absorption spectra were recorded on a Perkin Elmer Lambda 900 spectrophotometer. Fluorescence spectra were recorded on an Edinburgh Instruments FS920 double-monochromator spectrometer and a Peltier-cooled red-sensitive photomultiplier. Fluorescence lifetimes were determined using an Edinburgh Instruments LifeSpec-PS spectrometer, equipped with a 400 nm picosecond laser (PicoQuant PDL 800B) operated at 2.5 MHz and a Peltier-cooled Hamamatsu micro-channel plate photomultiplier (R3809U-50). Cyclic voltammograms were measured in 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as a supporting electrolyte in dichloromethane using a Potentioscan Wenking POS73 potentiostat. The working electrode was a Pt disk (0.2 cm^2), the counter electrode was a Pt plate (0.5 cm^2), and a saturated calomel electrode (SCE) was used as the reference electrode, calibrated against Fc/Fc$^+$ (+0.43 V).

N-(1-ethylpropyl)perylene-3,4:9,10-tetracarboxylic 3,4-anhydride 9,10-imide (2)

A mixture of *N,N′*-bis(1-ethylpropyl)perylene-3,4:9,10-tetracarboxylic diimide **1** (2.87 g, 5.4 mmol), potassium hydroxide (0.91 g, 0.016 mol) in *tert*-butanol (100 ml) was heated at 100 °C for 30 min. The reaction mixture was then poured into 400 ml of 10% HCl and the precipitate was filtered. The residue was stirred in 200 ml of a warm aqueous solution containing potassium hydroxide (20 g, 0.36 mol) and potassium chloride (16 g, 0.21 mol). The solid was filtered and subsequently washed with the aqueous solution until the solution was no longer coloured yellow–green. The solid was then stirred in water and subsequently filtered. The dark red coloured filtrate was precipitated by addition of hydrochloric acid to a final total percentage of 10% HCl concentration. The precipitate was filtered, washed with water and dried at 90 °C under vacuum to yield 0.50 g (20%) of a black solid. ^{1}H NMR (CDCl$_3$) δ 8.80–8.60 (m, 8H), 5.07 (m, 1H), 2.35–2.20 (m, 2H), 2.00–1.90 (m, 2H), 0.93 (t, *J* = 7.5 Hz). ^{13}C NMR (CDCl$_3$) δ 160.15, 136.61, 133.86, 133.76, 131.81, 124.10, 123.35, 123.24, 119.23, 58.03, 57.86, 25.16, 11.50, Electron impact MS: (MW = 461) *m*/*z* = 461.

N-(1-ethylpropyl)-*N′*-(4-amino-2,5-di-*tert*-butylphenyl)perylene-3,4:9,10-tetracarboxylic diimide (3)

A mixture of *N*-(1-ethylpropyl)perylene-3,4:9,10-tetracarboxylic 3,4-anhydride 9,10-imide **2** (0.048 g, 0.10 mmol), 2,5-di-*tert*-butylbenzene-1,4-diamine (0.14 g, 0.64 mmol), imidazole (2.5 g) and a few grains of zinc acetate were stirred at 160 °C for 3.5 h under argon. After cooling to room temperature the reaction mixture was purified extensively by column chromatography (SiO$_2$, CH$_2$Cl$_2$–ethanol 95 : 5, CH$_2$Cl$_2$–methanol 99 : 1–97.5 : 2.5, ethyl acetate–*n*-hexane 4 : 1 and ethyl acetate–*n*-hexane 3 : 2). After washing the solid with *n*-hexane 0.046 g (67%) of **3** was obtained pure as a red solid. ^{1}H NMR (CDCl$_3$) δ 8.80–8.65 (m, 8H), 6.87 (s, 1H), 6.82 (s, 1H), 5.08 (m, 1H), 3.93 (s, 2H), 2.40–2.20 (m, 2H), 2.10–1.90 (m, 2H), 1.54 (s, 18H), 0.94 (t, 6H, *J* = 7.3 Hz). ^{13}C NMR (CDCl$_3$) δ 164.88, 145.24, 145.07, 135.08, 134.71, 133.07, 131.99, 130.05, 129.79, 129.40, 126.96, 126.66, 124.02, 123.73, 123.31, 123.24, 118.18, 100.34, 57.92, 34.04, 31.76, 29.73, 25.21, 11.51. MALDI-TOF MS (MW = 663.31) *m*/*z* = 663.02 [M$^-$].

N-(1-ethylpropyl)-*N′*-{4-[2-ureido-6-(1-ethylpentyl)-4[1*H*]-pyrimidinone]-2′,5′-di-*tert*-butylphenyl}perylene-3,4:9,10-tetracarboxylic diimide (PERY-UP)

N-(1-ethylpropyl)-*N′*-(4-amino-2,5-di-*tert*-butylphenyl)perylene-3,4:9,10-tetracarboxylic diimide (**3**): (0.0262 g, 0.04 mmol) and *N*-[6-(1-ethylpentyl)-4-oxo-1,4-dihydropyrimidin-2-yl]-imidazolyl-1-carboxamide **4** (about 0.02 g, 0.07 mmol) were refluxed in dry chloroform (dried over molecular sieves) for 18 h under argon. After cooling to room temperature the reaction mixture was washed with 1M HCl (5 ml), saturated aqueous NaHCO$_3$, water, brine and was dried over Na$_2$SO$_4$. The product was triturated with acetone to yield 0.020 g (54%) of a red solid. ^{1}H NMR (CDCl$_3$)δ *two tautomers*: 13.27 (s, 1H), 12.59 (s, 1H), 11.67 (s, 1H), *minor 11.49 (s)*, 8.77 (d, 2H, *J* = 8.06 Hz), 8.69 (d, 2H, *J* = 8.06 Hz), 8.67 (d, 2H, *J* = 8.06 Hz), 8.66 (d, 2H, *J* = 8.06 Hz), *minor 7.63 (s)*, 7.47 (s, 1H), 7.10 (s, 1H), *minor 6.27 (s)*, 5.89 (s, 1H), 5.08 (m, 1H), *minor 2.53 (br s*), 2.45–2.10 (m, 3H), 1.98 (m, 2H), 1.80–1.50 (m, 4H), 1.44 (s, 9H), 1.30 (s, 13H), 1.00–0.80 (m, 12H). ^{13}C NMR (CDCl$_3$) δ *two tautomers*: 164.50, 156.06, 155.13, 145.53, 135.22, 134.61, 132.12, 130.07, 129.73, 126.94, 126.60, 123.69, 123.43, 123.27, 57.88, 45.43, 32.88, 31.68, 31.02, 29.41, 26.73, 25.15, 22.65, 14.03, 11.83, 11.57. MALDI-TOF MS (MW = 898.44). Found: *m*/*z* = 898.43 [M$^-$].

Pump-probe spectroscopy

The femtosecond laser system used for pump-probe experiments consists of an amplified Ti-sapphire laser (Spectra Physics Hurricane), providing 150 fs pulses at 800 nm with an energy of 750 μJ at 1 kHz. Pump (450 nm, fluence 0.5 μJ/mm^2) and probe (900 nm) pulses were created by optical parametric amplification followed by frequency quadrupling or doubling using two OPA's (Spectra Physics OPA-C). The pump beam was linearly polarized at the magic angle (54.7°) with respect to the probe beam. The temporal evolution was recorded using a Si detector and standard lock-in detection at 500 Hz.

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