JOURNAL OF
Materials
CHEMISTRY

Singlet-energy transfer in quadruple hydrogen-bonded oligo(*p*-phenylenevinylene)–fullerene dyads

Edwin H. A. Beckers,[a] Paul A. van Hal,[a] Albertus P. H. J. Schenning,[a] Abdelkrim El-ghayoury,[a] Emiel Peeters,[a] Minze T. Rispens,[b] Jan C. Hummelen,*[b] E. W. Meijer*[a] and René A. J. Janssen*[a]

[a]*Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands. E-mail: r.a.j.janssen@tue.nl*
[b]*Stratingh Institute and Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*

Received 31st January 2002, Accepted 17th April 2002
First published as an Advance Article on the web 9th May 2002

Two novel supramolecular dyads consisting of an oligo(*p*-phenylenevinylene) (OPV) donor and fullerene (C_{60}) acceptor are created *via* quadruple hydrogen bonding using self-complementary 2-ureido-4[1*H*]-pyrimidinone units. In the dyads, singlet-energy transfer from the excited OPV unit to the fullerene causes a strong quenching of the OPV fluorescence. The high association constant of the 2-ureido-4[1*H*]-pyrimidinone quadruple hydrogen-bonding unit results in high quenching factors ($Q_{\max} \geqslant 90$). The lower limit obtained for the rate constant for energy transfer ($k_{EN} \geqslant 6 \times 10^{10}$ s^{-1}) is rationalized in terms of the Förster mechanism. Photoinduced electron transfer does not occur in these hydrogen-bonded dimers, even in polar solvents. The absence of charge separation is ascribed to a low electronic coupling between the donor and acceptor in the excited state as result of the long distance between the chromophores.

Introduction

In nature, energy and electron transfer play a vital role in processes like *e.g.* photosynthesis[1] and respiratory oxidative phosphorylation.[2] The molecular interaction between the chromophores in these systems is based on supramolecular organization in which hydrogen bonding is often a key element.[3] To elucidate the influence of hydrogen bonding interaction on photophysical properties and mimic these biological superstructures, various studies were performed.[4–6] Systems containing multiple hydrogen bonds were designed to gain strength and directionality.[7] With respect to these multiple bonded assemblies, electron transfer has been reported in donor–acceptor systems linked by a two-fold hydrogen bonded salt[8] or acid[9] bridge as well as a two point binding *via* a hydroxyl/carbonyl interaction.[10] To create an even stronger binding between the chromophores, Sessler and co-workers used the triple hydrogen bonded Watson–Crick cytosine–guanine base pair in their studies.[11] In general, however, hydrogen-bonded donor–acceptor systems exhibit low association constants. Consequently, only a small fraction of the donor and acceptors remain associated, while the remaining molecules are free to diffuse in solution. To the best of our knowledge, the strongest hydrogen bonded donor–acceptor complex ($K_{\text{ass}} = 10^6$ M^{-1}) investigated in photoinduced electron transfer reactions has been reported by Hamilton and co-workers.[12]

The 2-ureido-4[1*H*]-pyrimidinone unit (Fig. 1) is a self-complementary DDAA motif quadruple hydrogen-bonding unit that possesses a high association constant of 6×10^7 M^{-1} in water-saturated chloroform.[13,14] In non-competitive solvents the association constant is believed to be even one order of magnitude higher. In addition to the quadruple hydrogen bonding, the dimerisation benefits from an intramolecular hydrogen bond present in the molecule. The high association constant enables the formation of supramolecular polymers[15,16] based on these systems and we recently reported on the formation of supramolecular hydrogen-bonded polymers carrying π-conjugated oligomers[17] and their incorporation into photovoltaic cells.[18]

Covalently linked dyads of oligo(*p*-phenylenevinylene)s (OPVs, Fig. 2) and [60]fullerene (C_{60}) exhibit interesting photophysical properties, among which energy and electron transfer reactions, and have been used to make photovoltaic devices.[19,20] Steady state fluorescence spectroscopy and sub-picosecond pump-probe spectroscopy established that photoexcitation of OPV4-C_{60} (Fig. 2) in apolar solvents, *e.g.* toluene, initiates an ultrafast (< 200 fs) intramolecular singlet-energy transfer from the photoexcited OPV4 unit to C_{60}.[21] In polar solvents, *e.g.* *o*-dichlorobenzene (ODCB), a photoinduced electron transfer occurs in OPV4-C_{60}, subsequent to the primary singlet-energy transfer, with a time constant of about 10 ps to yield a short-lived (~50–90 ps) charge-separated state.[21]

Supramolecular assembly of π-conjugated systems and fullerenes is a viable approach to create morphological organisation in the active layer of photovoltaic cells or to advance towards the complexity of natural photoactive systems. Various alternatives exist for assembling donor and acceptor molecules by weak molecular interactions. Recently, non-covalently linked zinc tetraphenylporphyrin–fullerene dyads *via* metal coordination have been described.[22] The focus of the present study is the formation and excited-state behaviour of a quadruple hydrogen bonded dyad involving an

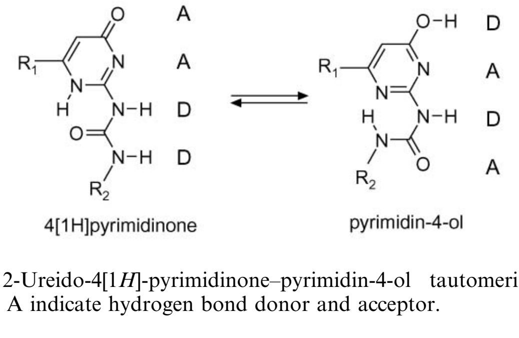

Fig. 1 2-Ureido-4[1*H*]-pyrimidinone–pyrimidin-4-ol tautomerisation. D and A indicate hydrogen bond donor and acceptor.

DOI: 10.1039/b201186g

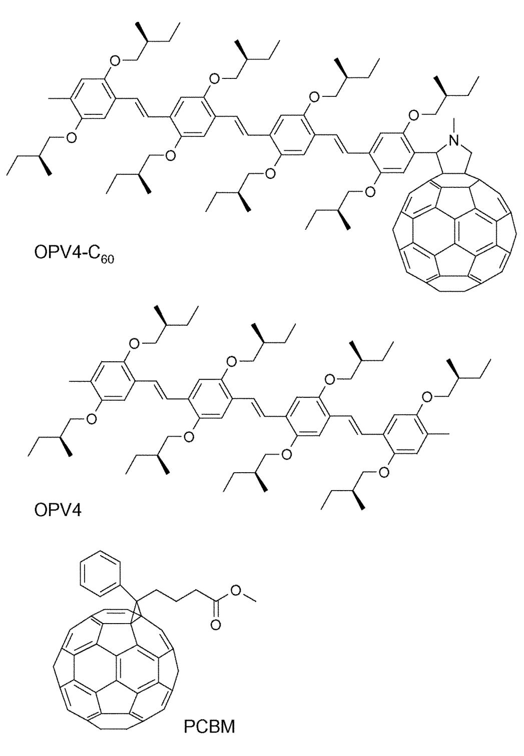

Fig. 2 Structures of OPV4-C_{60}, OPV4 and PCBM.

OPV4 donor and a C_{60} acceptor. As donor, two different OPV4 derivatives have been used (Fig. 3). The first (OPV4-UP1) consists of an OPV4 unit linked to the R^2 position *via* a methylene spacer, while the second (OPV4-UP2) has an OPV4 unit directly linked to the R^1 position of the ureidopyrimidinone moiety.[23] The acceptor is a fullerene derivative, linked to the R^2 position *via* a butyl spacer.[24]

The high fluorescence quantum yield of the OPV4-UP (OPV4-UP1 and OPV4-UP2) molecules in solution, together with the strong quadruple hydrogen bond, allows us to investigate photoinduced energy and electron transfer reactions at extremely low concentrations. The combination of a high binding constant and low concentrations in the experiments, minimizes collisional donor–acceptor interactions and the interference of free molecules present in solutions in photophysical experiments. In addition, the lifetime of the formed hydrogen bonded complexes ($>$ 100 milliseconds[14]) is significantly larger than the timescale for the expected photophysical processes. As a result, the true (static) properties of the supramolecular donor–acceptor complex in energy or electron transfer can be studied.

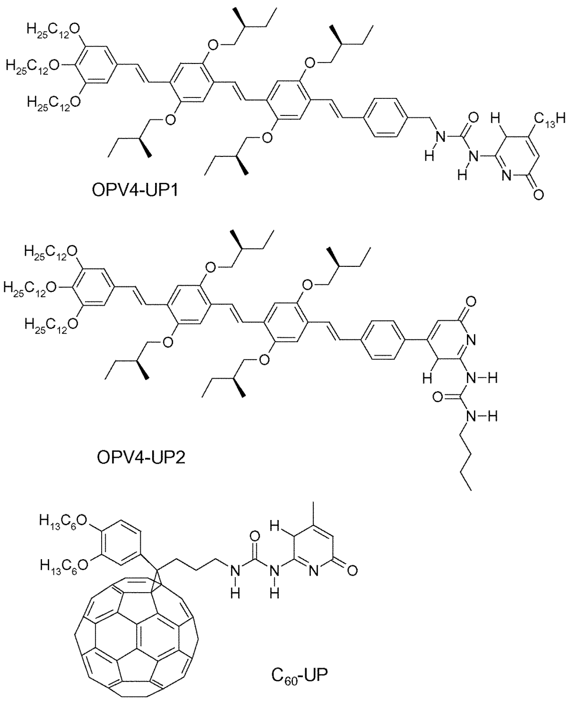

Fig. 3 2-Ureido-4[1H]-pyrimidinone OPV4-UP and C_{60}-UP compounds.

Experimental

General

Solvents were of AR (toluene, chloroform) or HPLC (ODCB) grade and were used as received. Proton NMR spectra were recorded on Varian 400 or 500 MHz spectrometers with TMS as an internal standard. UV/Vis absorption spectra were recorded on a Perkin Elmer Lambda 40 spectrometer.

Materials

The synthesis of the three ureidopyrimidinone compounds (OPV4-UP1, OPV4-UP2, and C_{60}-UP) used in this study has been described elsewhere.[23,24] OPV4[19] and PCBM[25] were used as reference compounds and were available from previous studies.

Fluorescence spectroscopy

Fluorescence spectra were recorded on a Perkin Elmer LS50B or an Edinburgh Instruments FS920 luminescence spectrometer. In the fluorescence quenching experiments, a stock solution of 10 ml 10^{-6} M OPV4-UP1 or OPV4-UP2 was used. To circumvent concentration corrections, 5 ml of this solution was used to dissolve the C_{60}-UP to give a 10^{-4} M C_{60}-UP solution with 10^{-6} M OPV4-UP. The first measurement to determine the I_0 fluorescence was measured on 2 ml of the OPV4-UP stock solution. The fluorescence signal I of OPV4-UP was then monitored upon addition of the OPV4-UP–C_{60}-UP solution in steps of first a few microliters and later steps of 100 to 250 µl. Finally the OPV4-UP–C_{60}-UP stock solution was measured in a separate experiment, providing the quenching in a 100 : 1 C_{60}-UP : OPV4-UP ratio. A cut-off filter of 665 nm was used in the emission beam to prevent stray light in the fluorescence experiments for detecting electron transfer.

For fluorescence quantum yield determination, solutions with an optical density of 0.1 at the excitation wavelength ($\lambda =$ 430 nm) were used and the spectra were corrected for the wavelength dependence of the detection system. The fluorescence spectra were integrated on an energy scale and the area was compared to that of a reference of fluorescein in 0.1 M aqueous NaOH with a quantum yield of 0.92.[27]

Fluorescence lifetimes

Time-correlated single photon counting fluorescence studies were performed on a home-built set-up and an Edinburgh Instruments LifeSpec-PS spectrometer. The first uses a mode-locked Ti:Sapphire laser, frequency doubled to obtain a 400 nm pulse, at a repetition frequency of 78 MHz. After dispersion by a 0.34 cm double monochromator, the fluorescence decay was recorded with time-correlated single photon counting in reversed mode using a Peltier-cooled Hamamatsu microchannel plate photomultiplier (R3809U-51). The LifeSpec-PS consists of a 400 nm picosecond laser (PicoQuant PDL 800B) operated at 2.5 MHz and a Peltier-cooled Hamamatsu microchannel plate photomultiplier (R3809U-50). Lifetimes were determined from the data using the Edinburgh Instruments software package.

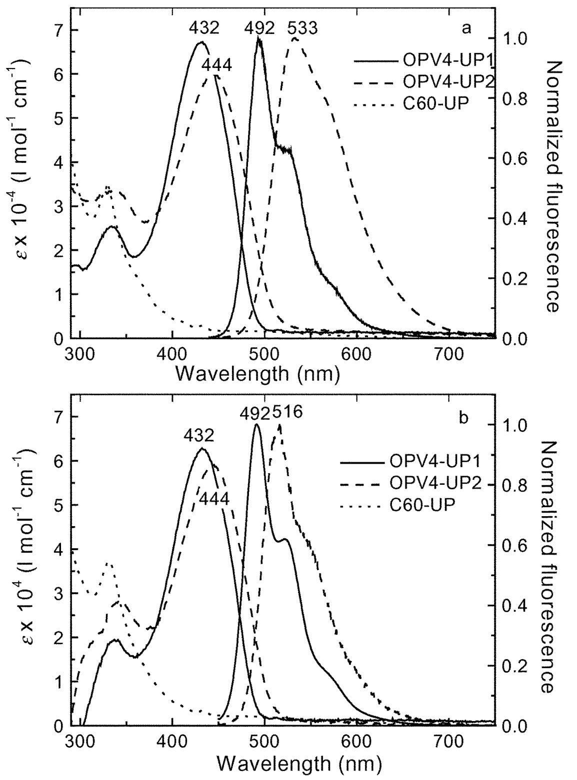

Fig. 4 Absorption and fluorescence spectra of OPV4-UP1, OPV4-UP2 and C_{60}-UP in chloroform (a) and toluene (b) (fluorescence of C_{60}-UP is not shown).

Results and discussion

Optical properties of OPV4-UP1 and OPV4-UP2

The UV/Vis absorption spectra of OPV4-UP1 and OPV4-UP2 are dominated by the strong π–π^* bands of the OPV4 unit in the 400–500 nm range (Fig. 4). The wavelength of maximum absorption of OPV4-UP2 shows a small, but significant, red shift of 12 nm compared to the spectrum of OPV4-UP1. This difference is attributed to the direct attachment of the OPV4 moiety to the isocytosine of the ureidopyrimidinone unit, resulting in a longer conjugation length.

Likewise, the fluorescence of OPV4-UP2 exhibits a red shift compared to that of OPV4-UP1 (Fig. 4). Surprisingly, the magnitude of the shift of the fluorescence spectrum depends on the solvent; it is more than 15 nm larger for chloroform than for toluene. In addition, the characteristic OPV4 emission, consisting of a strong 0–0 transition and a vibronic shoulder at longer wavelengths, as seen in toluene is transformed into a broad band in chloroform.

To investigate whether interactions between the two OPV4-UP molecules in the OPV4-UP homo-dimers, which are present under these conditions, may cause this effect, a titration with dimethyl sulfoxide (DMSO) was performed. DMSO is well known for its strong hydrogen bond accepting properties and addition of only a few percent of DMSO will break up any dimers and result in the sole presence of monomeric ureidopyrimidinone units. The fluorescence spectra of OPV4-UP1 in chloroform and toluene do not change upon addition of a small amount of DMSO (Fig. 5). This indicates that the absorption and fluorescence of monomeric and dimeric OPV4-UP1 are virtually identical. In contrast, when DMSO is added to an OPV4-UP2 solution, the fluorescence spectrum changes (Fig. 5). The spectrum in chloroform containing 0.2% (by volume) DMSO has shifted 10 nm to the blue and there is a small increase in fluorescence intensity. In toluene, both a shift and an increase in intensity were observed for OPV4-UP2, yet less pronounced than in the chloroform spectrum.[26] A tentative explanation for these effects is the formation of supramolecular assemblies of the homo-dimers as a result of π-stacking.[17] These supramolecular aggregates break up as soon as the quadruple hydrogen bonded homo-dimer dissociates by the addition of some DMSO.

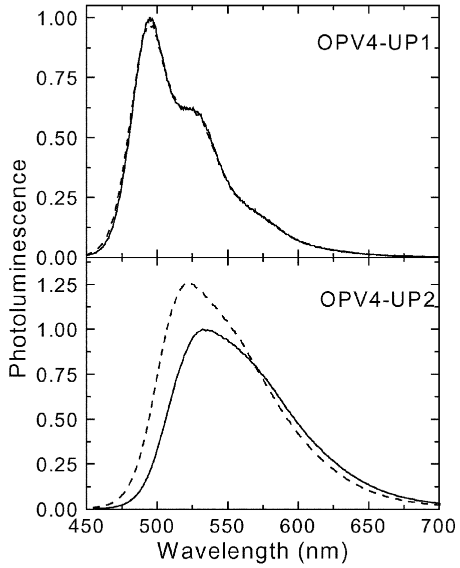

Fig. 5 Fluorescence of OPV4-UP in chloroform (solid line) and in chloroform with 0.2% DMSO (dashed lines), normalized to the concentration of the pure chloroform solutions.

The fluorescence quantum yield ϕ and lifetime τ of OPV4-UP1 and OPV4-UP2 were determined in the two solvents relative to fluorescein (ϕ = 0.92).[27] The quantum yield of OPV4-UP1 is slightly higher than that of OPV4-UP2, especially in chloroform (Table 1). The fluorescence quantum yield of OPV4-UP1, is similar to that of methyl end-capped OPV4 (Fig. 2) that is 0.80 and 0.74 in chloroform and toluene, respectively. Apparently the conjugation of the OPV4 moiety to the isocytosine of the ureidopyrimidinone unit in OPV-UP2, results in a small decrease of the quantum yield.

Fluorescence lifetimes, measured with time-correlated single photon counting are in the range of 1.23–1.58 ns and only slightly dependent on the solvent (Table 1).

Keto–enol equilibrium

Besides the 2-ureido-4[1*H*]-pyrimidinone, also referred to as the *keto* form, the pyrimidin-4-ol or *enol* tautomer can be present (Fig. 1). In case the R^1 substituent of the isocytosine moiety is a (substituted) phenyl group, the equilibrium shifts to the *enol* tautomer, especially in more apolar solvents like toluene.[13] An electron withdrawing R^1 substituent stabilizes the *enol* form because a proton on the nitrogen in the isocytosine is more acidic than a proton on the oxygen attached to the isocytosine.[28] The pyridin-4-ol tautomer represents a DADA motif, which has a lower association constant ($\sim 10^4$ to

Table 1 Percentage of 4[1*H*]-pyrimidinone (% *keto*) determined from ^{1}H NMR spectroscopy, the fluorescence lifetime (τ) and the fluorescence quantum yield (ϕ) in chloroform and toluene of OPV4-UP1, OPV4-UP2, and C_{60}-UP

Compound	Solvent	% *keto*	τ/ns	ϕ
OPV4-UP1	$CHCl_3$	> 99	1.54	0.88
	Toluene	90	1.23	0.84
OPV4-UP2	$CHCl_3$	85–90	1.58	0.59
	Toluene	~50	1.42	0.69
C_{60}-UP	$CHCl_3$	> 99	—	–
	Toluene	> 99	—	–

10^5 M^{-1}) due to less favourable secondary interaction in the hydrogen-bonding array.[13,29]

The DDAA and DADA motifs are not complementary and, hence, the equilibrium will affect the formation of the homo- and hetero-dimers. Therefore, it is important to determine the relative amount of both tautomeric forms present in solution. When both tautomers are present, the ^{1}H NMR spectra give two sets of three N–H protons.[13] In addition, the aromatic proton signal of the pyrimidin-4-ol tautomer is found 0.3–0.5 ppm downfield to the alkylidene proton signal of the 4[1*H*]-pyrimidinone tautomer.[13] By integration of the respective peak areas in the ^{1}H NMR spectra it is possible to determine the relative amounts of *keto* and *enol*. We found that in chloroform, OPV4-UP1 is solely present in the DDAA tautomeric form, while OPV4-UP2 contains some (10–15%) of the *enol* (Table 1). In toluene, the amounts of *keto* are less. OPV4-UP1 is 90% in the DDAA form in toluene, while the amount of 4[1*H*]-pyrimidinone in OPV4-UP2 has dropped to 50% (Table 1). The ^{1}H NMR spectrum of C_{60}-UP in toluene indicates that only the *keto* form is present. This is consistent with the fact that derivatives with *n*-alkyl substituents at both the R^1 and R^2 position are exclusively present as 4[1*H*]-pyrimidinone tautomers.[13] We have no indications that in the present case the *keto–enol* equilibrium depends on the concentration (at the concentrations measured by NMR), but previously the ratio of the two tautomers was found to be concentration-dependent, with the *enol* favoured at lower concentrations.[13] Hence, at lower concentrations, the actual ratios might differ from those collected in Table 1.

Fluorescence quenching

Fluorescence spectroscopy has been used to investigate the photophysical processes within the hydrogen bonded OPV4-UP–C_{60}-UP hetero-dimers after photoexcitation. Information on the rate for energy or electron transfer within a hetero-dimer can be obtained by monitoring the quenching of the photoluminescence of the OPV4-UP moiety upon addition of C_{60}-UP to an OPV4-UP solution. The reduction in photoluminescence is quantified by a quenching factor Q, defined as the ratio of the OPV4-UP fluorescence of the initial solution (I_0) and the OPV4-UP fluorescence of the OPV4-UP–C_{60}-UP mixture (I). The results are depicted in a modified Stern–Volmer[30] plot (Fig. 6), where the fluorescence quenching I_0/I is plotted as a function of the ratio of C_{60}-UP–OPV4-UP. Because an ultrafast singlet-energy transfer always precedes the electron transfer reaction in a covalently bound OPV4-C_{60} dyad in solution,[21] we focused on the energy transfer process first. To ensure that only *energy* transfer occurs from OPV4-UP to C_{60}-UP, rather apolar solvents as toluene (ε = 2.38) and chloroform (ε = 4.81) were used. To avoid contributions of OPV4-UP fluorescence quenching *via* dynamic processes (collisional quenching) and to minimize additional fluorescence from free OPV4-UP units (that are not bonded in a homo- or hetero-dimer), the total concentration of UP units was kept between 10^{-3} and 10^{-6} M. A control experiment using OPV4-UP2 and a soluble C_{60} derivative (PCBM, Fig. 2) that is not able to form hydrogen bonds, reveals that no quenching occurs under the experimental conditions (Fig. 7) and that dynamic (also referred to as collisional) quenching is not important. Consequently, the observed OPV4-UP photoluminescence only results from OPV4-UP–OPV4-UP homo-dimers and OPV4-UP–C_{60}-UP hetero-dimers. Hence, any quenching (Q) observed results from energy transfer in hetero-dimers only. It can be noted that a direct sensitisation of the fullerene fluorescence is not observable experimentally owing to the large excess of C_{60}-UP relative to the OPV4-UP donor.

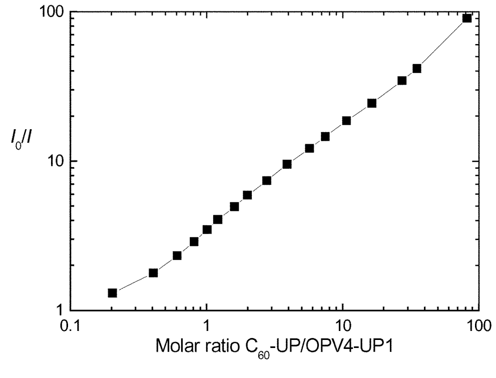

Fig. 6 Modified Stern–Volmer plot for the fluorescence quenching of OPV4-UP1 (10^{-6} M) in chloroform upon addition of C_{60}-UP. I_0 is the fluorescence signal of the pure OPV4-UP1 solution. The excitation wavelength is 432 nm; the fluorescence intensity (I) is determined at 492 nm.

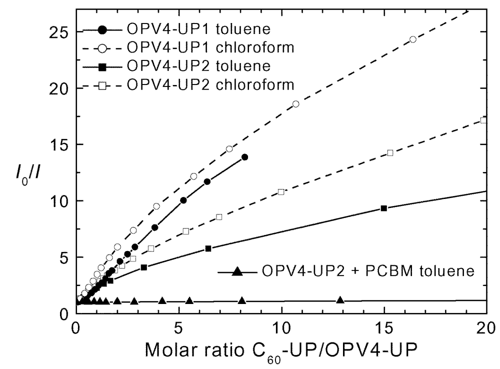

Fig. 7 Modified Stern–Volmer plot of fluorescence quenching in toluene and chloroform. Concentrations of OPV4-UP are constant at 10^{-6} M during the experiments. I_0 is the fluorescence signal of the pure OPV4-UP solution. The excitation wavelength is 432 nm; the fluorescence intensity (I) is determined at the emission maximum.

Fig. 6 shows that indeed a pronounced quenching of the OPV4-UP1 fluorescence occurs upon addition of C_{60}-UP to OPV4-UP1 in chloroform due to the supramolecular association of donor (OPV4-UP1) and acceptor (C_{60}-UP) moieties.[31] In the case of OPV4-UP1–C_{60}-UP in chloroform, a fluorescence quenching of $\geqslant$ 98.9% is obtained at the highest C_{60}-UP–OPV4-UP ratios investigated.[32] Interestingly, the Q value already exceeds the value of 2 at a C_{60}-UP : OPV4-UP1 ratio of 1 : 1. This indicates that there is a preference for the hetero-dimer, rather than a statistical distribution (1 : 2 : 1) of OPV4-UP homo-dimer : OPV4-UP–C_{60}-UP hetero-dimer : C_{60}-UP homo-dimer.[33] Without knowing the exact amounts present, the non-statistical distribution prevents an accurate estimate of the limiting quenching factor $Q_{\max}$ of a hetero-dimer. A lower limit of $Q_{\max}$, however, can be obtained from the amount of fluorescence quenching at large C_{60}-UP–OPV4-UP ratios ($>$50), where the excess of C_{60}-UP causes most OPV4-UP molecules to be attached to a C_{60}-UP molecule. In the case of OPV4-UP1–C_{60}-UP in chloroform, this results in $Q_{\max} \geqslant 90$. Since no limiting value of Q is reached upon addition of C_{60}-UP at large C_{60}-UP–OPV4-UP ratios (Fig. 6), the remaining fluorescence is predominated by the fluorescence of the OPV4-UP1–OPV4-UP1 homo-dimer rather than that of the OPV4-UP1–C_{60}-UP hetero-dimer. This lower estimate for $Q_{\max}$ is more than one order of magnitude larger than quenching factors previously reported for hydrogen-bonded donor–acceptor dyads.[8–12]

The fluorescence quenching of OPV4-UP1 upon addition of C_{60}-UP is less in toluene than in chloroform (Fig. 7). We ascribe this solvent effect to the *keto–enol* equilibrium discussed above. In chloroform, the amount of 4[1*H*]-pyrimidinone tautomer is higher than in toluene (Table 1). Because dimerisation is favoured for the *keto* form, the larger amount of 4[1*H*]-pyrimidinone in chloroform leads to a better coupling with the C_{60}-UP moiety and, hence, a more efficient quenching of the fluorescence.

The rationale that the amount of quenching is proportional to the amount of *keto* form present, is supported by the fluorescence quenching experiments on OPV4-UP2 in chloroform and toluene upon addition of C_{60}-UP. For OPV4-UP2 the amount of *keto* is much less in toluene (50%) than in chloroform (85–90%, Table 1). Accordingly, the quenching of the OPV4-UP2 fluorescence in chloroform is almost double that in toluene.

Nevertheless, there is a remarkable difference in the amount of quenching of OPV4-UP1 and OPV4-UP2 in both solvents (Fig. 7). Even in chloroform, where the *keto* form is the dominant tautomer, the fluorescence of OPV4-UP1 is quenched to a significantly larger extent than that of OPV4-UP2 upon adding C_{60}-UP. While it is clear that the difference must originate from a difference in molecular structure, the remarkable observation is that the distance between donor and acceptor is larger in the OPV4-UP1–C_{60}-UP dimer than in the OPV4-UP2–C_{60}-UP dimer, while the latter has a lower quenching factor.

The fluorescence quenching experiments of the OPV4-UP1 and OPV4-UP2 using C_{60}-UP afford the quenching factors at different ratios of quencher *versus* fluorophore. We have shown that these values are directly related to the dimerisation equilibrium of the hydrogen bonding molecules, their opportunity to form hetero- or homo-couples and the *keto–enol* equilibrium of the individual chromophores. Although in principle it is possible to extract equilibrium constants and $Q_{\max}$ from the Stern–Volmer plots, the complex nature of the system caused by the great variety of species present, hampered us in achieving this goal.

Förster energy transfer

With the values of ϕ and τ the rate for singlet-energy transfer between a donor and acceptor can be estimated according using the Förster equation.[34]

$$k_{EN} = \frac{1}{\tau}\cdot\frac{9000(\ln 10)\frac{2}{3}\phi}{128\pi^5 N_{av} n^4 d^6} J_F \tag{1}$$

In eqn. (1), the parameters N_{av} and n represent Avogadro's number and the refractive index of the solvent. The value of d is the centre-to-centre distance of the two chromophores involved in the energy transfer. This calculation uses the overlap (J_F) between the absorption ($\varepsilon(\bar{\nu})$) of the acceptor (C_{60}-UP) and the fluorescence ($F(\bar{\nu})$) of the donor (OPV4-UP) on an energy scale (cm^{-1}) defined as:

$$J_F = \frac{\int\left(\frac{F(\bar{\nu})\varepsilon(\bar{\nu})}{\bar{\nu}^4}\right)d\bar{\nu}}{\int F(\bar{\nu})d\bar{\nu}} \tag{2}$$

In addition, the rate for singlet-energy transfer can be obtained experimentally from the lifetime τ and $Q_{\max}$ *via*:

$$k_{EN} = \frac{Q_{\max} - 1}{\tau} \tag{3}$$

Using the lower estimate of $Q_{\max} \geqslant 90$ obtained for the OPV4-UP1–C_{60}-UP hetero-dimer, a rate constant for singlet-energy transfer of $k_{EN} \geqslant 6 \times 10^{10}\ \mathrm{s}^{-1}$ is obtained from eqn. (3), which according to eqn. (1) corresponds to $d \leqslant 17$ Å. Using molecular modelling a distance of 18–19 Å has been estimated between the centre of the fullerene and the centre of the first phenyl ring of the OPV unit, *i.e.* close to the estimate of 17 Å based on the Förster model. It is interesting to note that in a previous study on OPV4-C_{60} (Fig. 2) a similar conclusion was reached.[21] For covalently linked OPV4-C_{60} we established that delocalisation of the singlet-excited state onto the first benzene ring of the OPV4 unit is indeed a requirement to explain the high rate for singlet-energy transfer of $k_{EN} = 5.3 \times 10^{12}\ \mathrm{s}^{-1}$ in this dyad by the Förster mechanism.[21]

Electron transfer

After having assessed the occurrence of *energy* transfer within the two OPV4-UP–C_{60}-UP hetero-dimers, it is of interest to see if photoinduced *electron* transfer occurs in these hydrogen-bonded dyads. For OPV4-C_{60}, the occurrence of an electron transfer reaction depends strongly on the polarity of the solvent.[20,21] This solvent dependence could be explained quantitatively by the Weller equation, which relates the change in free energy for charge separation (G_{GS}) to the polarity (ε_{S}) of the solvent:[35]

$$\begin{aligned} G_{\mathrm{cs}} = {} & e(E_{\mathrm{ox}}(\mathrm{D}) - E_{\mathrm{red}}(\mathrm{A})) - \frac{e^2}{4\pi\varepsilon_0\varepsilon_{\mathrm{s}}R_{\mathrm{cc}}} \\ & - \frac{e^2}{8\pi\varepsilon_0}\left(\frac{1}{r^+} + \frac{1}{r^-}\right)\left(\frac{1}{\varepsilon_{\mathrm{ref}}} - \frac{1}{\varepsilon_{\mathrm{s}}}\right) \end{aligned} \tag{4}$$

Here $-e$ is the electron charge, ε_0 is the vacuum permittivity, $\varepsilon_{\mathrm{ref}}$ the polarity of the solvent used to determine the redox potentials $E_{\mathrm{ox}}(\mathrm{D})$ and $E_{\mathrm{red}}(\mathrm{A})$, R_{cc} the centre-to-centre distance of positive and negative charges, and r^+ and r^- the radii of the positive and negative ions.[19] Using eqn. (4), G_{GS} was determined for the OPV4-UP1 ($E_{\mathrm{ox}}(\mathrm{D}) = 0.71$ V *vs.* SCE) and C_{60}-UP ($E_{\mathrm{red}}(\mathrm{A}) = -0.67$ V *vs.* SCE) combination (Fig. 8). In this calculation, the centre-to-centre distance between donor and acceptor was set at the minimum value possible for hydrogen-bonded hetero-dimer ($R_{\mathrm{cc}} = 17$ Å) and at infinity (energetically most unfavourable). The decrease of G_{CS} with increasing polarity of the solvent results in a negative value for ΔG_{CS} for charge separation relative to the singlet and triplet excited state of C_{60}-UP in polar solvents like ODCB and benzonitrile, irrespective of R_{cc}. Hence, from a free-energy point of view, electron transfer is possible in ODCB, but the actual rate will depend on the electronic coupling between the donor and acceptor in the excited state.

The formation of a charge-separated state can be identified experimentally from a quenching of the acceptor fluorescence. When C_{60}-UP is excited in the presence of OPV4-UP1, electron transfer should result in a quenching of the fullerene fluorescence, relative to the signal of a solution containing only C_{60}-UP.

In the hydrogen bonded OPV4-UP1–C_{60}-UP system in ODCB, this quenching of the C_{60}-UP emission is not detected (Fig. 9, top). A small blue shift of the C_{60}-UP emission is observed, probably due to an unknown impurity. A titration experiment (Fig. 9, bottom), monitoring the OPV4-UP1 fluorescence, resulted in a similar quenching as in apolar solvents, indicating that the hydrogen bonded hetero-dimer is formed in ODCB and undergoes singlet-energy transfer after photoexcitation. The OPV4-UP1 fluorescence quenching in ODCB occurs to the same extent as in toluene and chloroform.

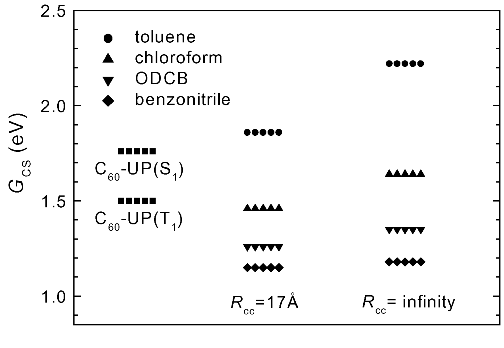

Fig. 8 The Gibbs-free energy of the charge-separated state of the OPV4-UP1–C_{60}-UP couple in solvents of different polarity, calculated using eqn. (4) assuming a centre-to-centre distance between positive and negative charges of 17 Å (in the hydrogen bonded dimer) and infinity (upper limit). At the left side the singlet (S_1) and triplet (T_1) levels of C_{60}-UP are shown.

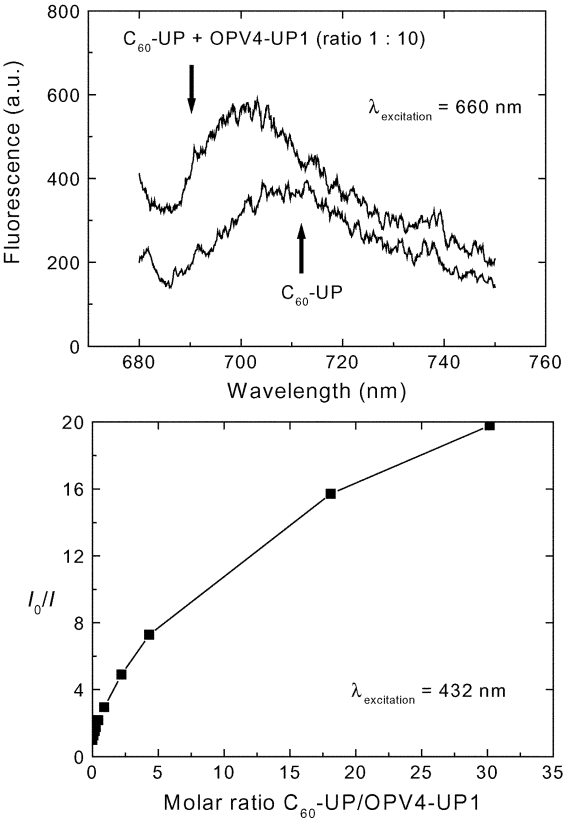

Fig. 9 Fluorescence quenching for OPV4-UP1–C_{60}-UP solutions in ODCB. The C_{60}-UP concentration is 4×10^{-5} M for the top graph. The OPV4-UP1 concentration for the experiment shown in the bottom graph is 10^{-6} M.

An explanation for the possible absence of charge transfer between OPV4-UP1 and C_{60}-UP can be found in the larger distance over which the transfer must take place compared to OPV4-C_{60}. The large distance between the donor and the acceptor induced by the two ureidopyrimidinone units and the exponential decay of electron transfer rates with increasing distance,[36] results in a reduced tendency for charge transfer.[37]

Conclusion

We have shown that photoinduced singlet-energy transfer between OPV4 and C_{60} derivatives is possible in 2-ureido-4[1*H*]-pyrimidinone hydrogen bonded hetero-dimers in apolar and polar solvents. The change in the equilibrium between 4[1*H*]-pyrimidinone and pyrimidin-4-ol tautomers of OPV4-UP by varying the solvent, results in a proportional change in the quenching factor of the OPV4-UP fluorescence because the *enol* form is not able to bind with the *keto* form of C_{60}-UP. The lower limit of the maximum quenching ($Q_{\max} \geqslant 90$) obtained for OPV4-UP1–C_{60}-UP mixtures in chloroform is at least one order of magnitude higher than values reported so far for hydrogen-bonded dyads[8–12] and results from the high association constant of the dimers.[14] $Q_{\max} \geqslant 90$ corresponds to a rate constant for singlet-energy transfer of $k_{EN} \geqslant 6 \times 10^{10}$ s^{-1} which can be rationalized based on the Förster mechanism. Although energetically possible, photoinduced electron transfer does not occur in these hydrogen-bonded dimers. The absence of charge separation in polar solvents is most likely due to the significant distance between donor and acceptor in the quadruple hydrogen-bonded hetero-dimers that causes an exponential decrease in the electronic coupling between the two units in the excited state.

Acknowledgement

This work was financially supported by the Dutch Ministry of Economic Affairs, the Ministry of Education, Culture and Science, and the Ministry of Housing, Spatial Planning and the Environment through the E.E.T. program (EETK97115), and by the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (CW-NWO) and the Eindhoven University of Technology in the PIONIER program (98400).

References

1 (*a*) C. C. Moser, J. M. Keske, K. Warnecke, R. S. Farid and P. L. Dutton, *Nature*, 1992, **355**, 796; (*b*) M. R. Wasielewski, *Chem. Rev.*, 1992, **92**, 435.
2 (*a*) H. Pelletier and J. Kraut, *Science*, 1992, **258**, 1748; (*b*) T. Hayashi and H. Ogoshi, *Chem. Soc. Rev.*, 1997, **26**, 355.
3 J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995.
4 V. Balzani and F. Scandola, *Supramolecular Photochemistry*, Ellis Horwood, Chichester, 1991.
5 P. Piotrowiak, *Chem. Soc. Rev.*, 1999, **28**, 143.
6 J. L. Sessler, B. Wang, S. L. Springs and C. T. Brown, in *Comprehensive Supramolecular Chemistry*, ed. J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle and Y. Murakami, Pergamon, Oxford, 1996, Vol. 4, p. 311.
7 (*a*) P. S. Corbin and S. C. Zimmermann, *J. Am. Chem. Soc.*, 1998, **120**, 9710; (*b*) J. L. Sessler and R. Wang, *Angew. Chem., Int. Ed.*, 1998, **37**, 1726; (*c*) D. C. Sherrington and K. A. Taskinen, *Chem. Soc. Rev.*, 2001, **30**, 83.
8 (*a*) J. A. Roberts, J. P. Kirby and D. G. Nocera, *J. Am. Chem. Soc.*, 1995, **117**, 8051; (*b*) J. P. Kirby, J. A. Roberts and D. G. Nocera, *J. Am. Chem. Soc.*, 1997, **119**, 9230; (*c*) A. J. Myles and N. R. Branda, *J. Am. Chem. Soc.*, 2001, **123**, 177.
9 (*a*) C. Turro, C. K. Chang, G. E. Leroi, R. I. Cukier and D. G. Nocera, *J. Am. Chem. Soc.*, 1992, **114**, 4013; (*b*) E. Prasad and K. R. Gopidas, *J. Am. Chem. Soc.*, 2000, **122**, 3191; (*c*) M. A. Smitha, E. Prasad and K. R. Gopidas, *J. Am. Chem. Soc.*, 2001, **123**, 1159; (*d*) M. A. Smitha and K. R. Gopidas, *Chem. Phys. Lett.*, 2001, **350**, 86.
10 Y. Aoyama, M. Asakawa, Y. Matsui and H. Ogoshi, *J. Am. Chem. Soc.*, 1991, **113**, 6233.
11 (*a*) H. Furuta, D. J. Magda and J. L. Sessler, *J. Am. Chem. Soc.*, 1991, **113**, 978; (*b*) A. Harriman, D. J. Magda and J. L. Sessler, *J. Phys. Chem.*, 1991, **95**, 1530; (*c*) A. Harriman, Y. Kubo and J. L. Sessler, *J. Am. Chem. Soc.*, 1992, **114**, 388; (*d*) J. L. Sessler, B. Wang and A. Harriman, *J. Am. Chem. Soc.*, 1993, **115**, 10418; (*e*) J. L. Sessler, M. Sathiosatham, C. T. Brown, T. A. Rhodes and G. Wiederrecht, *J. Am. Chem. Soc.*, 2001, **123**, 3655.
12 P. Tecilla, R. P. Dixon, G. Slobodkin, D. S. Alavi, D. H. Waldeck and A. D. Hamilton, *J. Am. Chem. Soc.*, 1990, **112**, 9408.
13 F. H. Beijer, H. Kooijman, A. L. Spek, R. P. Sijbesma and E. W. Meijer, *J. Am. Chem. Soc.*, 1998, **37**, 75.
14 S. H. M. Söntjens, R. P. Sijbesma, M. H. P. van Genderen and E. W. Meijer, *J. Am. Chem. Soc.*, 2000, **122**, 7487.
15 R. P. Sijbesma, F. H. Beijer, L. Brunsveld, B. J. B. Folmer, J. H. K. K. Hirschberg, R. F. M. Lange, J. K. L. Lowe and E. W. Meijer, *Science*, 1997, **278**, 1601.
16 L. Brunsveld, B. J. B. Folmer, E. W. Meijer and R. P. Sijbesma, *Chem. Rev.*, 2001, **101**, 4071.
17 A. P. H. J. Schenning, P. Jonkheijm, E. Peeters and E. W. Meijer, *J. Am. Chem. Soc.*, 2001, **123**, 409.
18 A. El-ghayoury, A. P. H. J. Schenning, P. A. van Hal, J. K. J. van Duren, R. A. J. Janssen and E. W. Meijer, *Angew. Chem., Int. Ed.*, 2001, **40**, 3660.
19 (*a*) J.-F. Nierengarten, J.-F. Eckert, J.-F. Nicoud, L. Ouali, V. Krasnikov and G. Hadziioannou, *Chem. Commun.*, 1999, 617; (*b*) J.-F. Eckert, J.-F. Nicoud, J.-F. Nierengarten, S.-G. Liu, L. Echegoyen, F. Barigelletti, N. Armaroli, L. Ouali, V. Krasnikov and G. Hadziioannou, *J. Am. Chem. Soc.*, 2000, **122**, 7467; (*c*) N. Armaroli, F. Barigelletti, P. Ceroni, J.-F. Eckert, J.-F. Nicoud and J.-F. Nierengarten, *Chem. Commun.*, 2000, 599.
20 E. Peeters, P. A. van Hal, J. Knol, C. J. Brabec, N. S. Sariciftci, J. C. Hummelen and R. A. J. Janssen, *J. Phys. Chem. B.*, 2000, **104**, 10174.
21 P. A. van Hal, R. A. J. Janssen, G. Lanzani, G. Cerullo, M. Zavelani-Rossi and S. De Silvestri, *Phys. Rev. B*, 2001, **64**, 075206.
22 (*a*) N. Armaroli, F. Diederich, L. Echegoyen, T. Habicher, L. Flamigni, G. Marconi and J.-F. Nierengarten, *New. J. Chem.*,

1999, **23**, 77; (*b*) F. Dsouza, G. R. Deviprasad, M. S. Rahman and J. P. Choi, *Inorg. Chem.*, 1999, **38**, 2157; (*c*) T. Da Ros, M. Prato, D. Guldi, E. Alessio, M. Ruzzi and L. Pasimeni, *Chem. Commun.*, 1999, 635; (*d*) D. Guldi, C. Luo, T. Da Ros, M. Prato, E. Dietel and A. Hirsch, *Chem. Commun.*, 2000, 375.

23 A. El-ghayoury, E. Peeters, A. P. H. J. Schenning and E. W. Meijer, *Chem. Commun.*, 2000, 1969.

24 M. T. Rispens, L. Sánchez, J. Knol and J. C. Hummelen, *Chem. Commun.*, 2001, 161.

25 J. C. Hummelen, B. W. Knight, F. LePeq, F. Wudl, J. Yao and C. L. Wilkins, *J. Org. Chem.*, 1995, **60**, 532.

26 All spectra shown are 0.2% DMSO solutions by volume. Spectra of solutions containing 0.1% to 0.5% are similar, above 1% DMSO the spectra change due to polarity increase of the solvent mixture and a possible presence of a non-hydrogen bonding *keto* believed to exist in DMSO, see F. H. Beijer, *Ph.D. Thesis*, Eindhoven University of Technology, 1998.

27 J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 991.

28 J. Elguero, C. Marzin, A. R. Katritzky and P. Linda, *Advances in Heterocyclic Chemistry, the Tautomerism of Heterocycles*, Academic Press, New York, 1976.

29 (*a*) W. L. Jorgensen and J. Pranata, *J. Am. Chem. Soc.*, 1990, **112**, 2008; (*b*) J. Pranata, S. G. Wierschke and W. L. Jorgensen, *J. Am. Chem. Soc.*, 1991, **113**, 2810.

30 O. Stern and M. Volmer, *Phys. Z.*, 1919, **20**, 183.

31 The supramolecular association of the donor and acceptor was also observed in a ^{1}H NMR spectrum of a mixture of both chromophores.

32 At the highest C60-UP concentration, the OPV4-UP1 quenching might be overestimated somewhat because the excitation (432 nm) also excites C60-UP.

33 In a 1 : 1 mixture of two compounds A and B, the statistical ratio for the formation of dimers is 1 : 2 : 1 for A–A : A–B : B–B.

34 T. Förster, *Discuss. Faraday Soc.*, 1959, **27**, 7.

35 A. Weller, *Z. Phys. Chem.,Neue Folge*, 1982, **133**, 93.

36 M. R. Wasielewski, in Photoinduced Electron Transfer, ed. M. A. Fox and M. Chanon, Vol 1, pp 161–206.

37 R. Pati and S. P. Karna, *Chem. Phys. Lett.*, 2002, **351**, 302.