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Light-Driven Charge Separation in Isoxazolidine–Perylene Bisimide Dyads

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Abstract: A series of arrays for lightdriven charge separation is presented, in which perylene tetracarboxylic bisimide is the light-absorbing chromophore and electron acceptor, whereas isoxazolidines are colourless electron donors, the electron-releasing properties of which are increased with respect to the amino group by means of the α - effect. Charge separation (CS) in toluene over a distance ranging from ≈ 10 to ≈ 16 Å, with efficiencies of ≈ 95 to

Keywords: charge separation • charge transfer • electron transfer • photochemistry • supramolecular chemistry \approx 50% and CS lifetimes from 300 ps to 15 ns, are demonstrated. In dichloromethane the charge recombination reaction is faster than charge separation, preventing accumulation of the CS state. The effects of solvent polarity and molecular structure are discussed in the frame of current theories.

Introduction

Light-driven charge separation is attaining increasing interest, because it represents the key step for exploitation of solar energy in different applications, such as organic photovoltaic cells,^[1] photoelectrochemical cells (DSSC)^[2] and artificial photosynthesis.^[3] Organic materials are very attractive for such applications because of easy variability, high colour strengths, unproblematic recycling and easy processing. Suitable chromophores are required because sunlight has to be efficiently absorbed, promoting the ground state molecule into the excited state, which is the "reagent" of a photochemical reaction. Thus, an electron hole (defect electron) is generated in the HOMO, and a single electron is left in the LUMO in the initial step. These must be detached in a subsequent charge-separating step. There are two possibilities for this step. Firstly, one can move the excited electron away from the LUMO of the chromophore to some other molecular entity; this means a light-driven oxidation of the excited

dye. Secondly, one can fill the electron hole in the HOMO with an external electron; this means a light-driven reduction of a singlet excited state. The reduction of the excited state is the subject of this investigation.

We have selected perylene tetracarboxylic bisimides^[4] (1) as the light-absorbing chromophore, because of their extra-



ordinarily high photostability, their strong absorption in the visible range of the spectrum and their high fluorescence quantum yield,^[5] which allows the use of luminescence techniques to monitor the early events in the photoreaction. This chromophore is moderately electron-depleted owing to the four carbonyl groups, and the linking to an electron-rich structure may induce a light-driven electron transfer. In fact perylene bisimide **1** and closely related chromophores have been extensively used as electron acceptors in molecular arrays for photoinduced charge separation.^[6] In comparison to other typical electron acceptors for photoinduced charge separation such as fullerenes, this chromophore is characterised by a radical anion with intense and characteristic absorption features in the visible–NIR region.^[7] The radical absorption is also very different from that of the singlet ex-

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cited state, allowing precise and unambiguous identification of the electron-transfer step.^[8]

We have been focussing on new compounds as possible electron donors. Such structures should be colourless, to avoid interference with the light absorption of the chromophores and to allow a simple mechanistic study of the system. The attachment of a simple amino group to the nitrogen atoms in its function as an electron-rich structure is sufficient to cause fluorescence quenching by electransfer.^[9] tron However. charge will still remain close to the chromophore in such structures and is not expected to lead to a sufficiently stable charge-separated state. Unfortunately, a further separation of the amino group from the chromophore by means of an aliphatic spacer proved not to be useful, because the electron transfer is stopped and very high fluorescent quantum yields were observed for such amino derivatives.^[10] Thus, we tried to improve the electron-donating properties of the amino group by the application of the α effect; compare reference [11].



Scheme 1. Synthesis of the nitrones 3 and 4 and reaction of 4 with styrene to form the isoxazolidines 5a and 5b.

An oxygen atom directly linked to the aliphatic amine would be a suitable element of structure. However, such hydroxyl amines are comparably labile. Their incorporation into a ring structure would improve the stability. As a consequence, we targeted the synthesis of isoxazolidines to be used as electron donors in perylene-bisimide-based dyads for charge separation.

Results and Discussion

Design and synthesis: We started synthesis with the aldehyde^[12] **2** and condensed it to form the nitrone **3** as a key intermediate for the synthesis of isoxazolidines by 1,3-dipolar cycloaddition.^[13] However, no reaction of **3** was observed with olefins such as styrene. Thus, we prepared the more reactive^[14] *N*-phenyl nitrone **4** by the condensation of **2** with *N*-phenyl hydroxylamine. The cycloaddition was successful with an excess of styrene to form the isoxazolidines **5a** and **5b** as a pair of diastereomers with very similar properties (see Scheme 1). Analogously, the nitrone **4** reacts with methyl methacrylate to form a single diastereomer **6**; evidently, the steric demand of the substituents at the fivemembered ring do not allow the other regio-constellations (see Scheme 2). The same effect holds for crotonic ester (formation of compound 7). On the other hand, the steric demand of acrylonitrile is so low that the two regio-isomers 8 and 9 were obtained.

We aimed to lengthen the spacer between the chromophore and the isoxazolidine for a more distant charge separation by a further phenyl group. Therefore, we condensed the aldehyde 10 with N-methyl hydroxyl amine and obtained the nitrone 11 with a biphenyl spacer (see Scheme 3). However, no reaction proceeded with styrene, although the reacting nitrone group is farther from the chromophore than in 5. We tried to prepare a phenyl nitrone with a biphenyl spacer analogously to 4 by the condensation of 10 with phenyl hydroxylamine in order to increase the reactivity. However, this phenyl nitrone could not be isolated from the reaction mixture because of instability. On the other hand, a condensation of 10 with phenyl hydroxylamine in the presence of an excess of styrene allowed the intermediate nitrone to be trapped, and the diastereomers 12a and 12b, exhibiting very similar properties, to be obtained.

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Spectroscopy and photophysics: The photoreactivity of synthesised isoxazolidine dyads has been determined in comparison with the perylenebisimide (**PI**) and isoxazolidine (**IA**) models. We studied the dyads **5–7** and **12**, and models **IA5–7** and **IA12** (shown in Schemes 1, 2, and 4), and



Scheme 2. Synthesis of the dyads 6-9.

Figure 1 shows a 3D representation of dyad 12. Two solvents have been used for the photophysical experiments: low polarity toluene, and medium polarity dichloromethane, in view of the expected effect of polarity on the possible charge-transfer reactions. The absorption spectra of PI in the two solvents are very similar, except for a 2-3 nm hypsochromic shift in the maxima in dichloromethane. The absorption of a few representative dyads in toluene are reported in Figure 2 together with the spectra of the PI model. They are identical above 400 nm, and are only slightly bathochromically shifted by 0.5 nm compared with PI, whereas slight differences are seen in the UV, more pronounced for 12 because of the absorption of the biphenyl spacer. The absorption of IA is in the UV; however, in the present work only the visible region is considered and the PI chromophore is the only photoactive component. Covalent binding of isoxazolidine units has a very modest effect on the spectroscopic properties of PI in the dyad, indicating an efficient electronic decoupling of the chromophore in the ground state from the attached heterocyclic ring as a consequence both of insulating aliphatic carbon atoms, and of the linking



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Scheme 3. Synthesis of the nitrone 11 and the dyads 12a and 12b.



Scheme 4.



Figure 1. Calculated structure of a derivative of 12.

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Figure 2. Absorption spectra in toluene of PI (grey), 7 (black line), and 12 (dashed line).

to the nitrogen atom where orbital nodes are in the HOMO and LUMO.^[15] This allows a study of the properties of the dyads with reference to the property of the isolated models, and permits, by comparison, the determination of the intramolecular processes taking place in the assembly.

The luminescence of PI in toluene is slightly reduced $(\phi_{\rm fl}=0.92)$ compared to that in dichloromethane $(\phi_{\rm fl}=$ 0.99)^[5] and, in agreement with the absorption spectra, the fluorescence maxima are shifted to higher energies by \approx 3 nm in dichloromethane. The luminescence of **PI** in the dyads is quenched, as shown in Figure 3 for the two solvents. Excitation in the PI bands of optically matched solutions of the dyad 12 in toluene leads to a somehow reduced quenching compared to dichloromethane; it is in fact quenched to 46% in toluene and to 22% in dichloromethane, whereas dyads 7, 5, and 6 are quenched to a similar extent in both solvents: 20% for 7 and 10% for 5 and 6. The luminescence parameters of the dyads and of the model PI are collected in Table 1; it can be seen that the position of the PI luminescence bands is essentially unaffected after binding of IA. Luminescence spectra at 77 K (data not shown) indicate a reduced quenching in the dyads with respect to PI compared to that at room temperature. We are conscious that the 77 K data cannot be interpreted quantitatively for the geometrical conditions of the experiment (see the Experimental Section), however, they suggest that the quenching process of PI luminescence is blocked or reduced in a rigid environment.

The lifetime of the **PI** chromophore, which is 4.0 ns in toluene and 4.1 ns in dichloromethane, is greatly reduced in



Figure 3. Room-temperature emission spectra of optically matched solutions of **PI** (grey), **5** (full circles), **6** (dashed line), **7** (black line), **12** (dots). A = 0.24, excitation at 488 nm for dichloromethane (bottom) and 490 nm for toluene (top).

the dyads to values ranging from 2.3 to 0.25 ns in toluene and from 1.04 to 0.24 ns in dichloromethane (Table 1). The time-resolved luminescence decays of 12 and 5 in both solvents are displayed in Figure 4. The reduction in lifetime



Figure 4. Time evolution of the luminescence registered at 650 nm from dyads after excitation with a laser pulse (35 ps, 532 nm, 1 mJ), grey in toluene and black in dichloromethane: **12** (line), **5** (full circles).

Table 1. Luminescence properties of !	PI model and dyads in toluene and	I dichloromethane at room tem	perature and in toluene solutions at 77 K
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	298 K					77 K			
	Toluene			Dichloromethane			Toluene		
	λ_{\max} [nm]	$arPsi_{ m fl}{}^{[m a]}$	$\tau \text{ [ns]}^{[b]}$	λ_{\max} [nm]	$arPsi_{ m fl}{}^{[m a]}$	$\tau \ [ns]^{[b]}$	λ_{\max} [nm]	$\tau \text{ [ns]}^{[b]}$	$E [\mathrm{eV}]^{[\mathrm{c}]}$
PI	534, 574, 622	0.92	4.0	531, 571, 619	0.99	4.1	543, 587, 638	4.6	2.3
5	535, 576, 621	0.10	0.29	532, 573, 618	0.10	0.25	543, 585, 637	2.6	2.3
6	535, 576, 621	0.10	0.25	532, 573, 618	0.10	0.24	543, 585, 637	3.4	2.3
7	535, 576, 621	0.19	0.55	533, 573, 618	0.19	0.52	543, 586, 637	4.7	2.3
12	536, 576, 622	0.425	2.3	533, 573, 618	0.22	1.04	542, 584, 638	4.5	2.3

[a] Fluorescence quantum yield. [b] Lifetime of the singlet excited state localised on **PI**; excitation is at 532 nm for the picosecond range and at 465 nm for the nanosecond range. [c] Excited state energy levels derived from the 77 K emission maxima.



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parallels reasonably well the reduction in luminescence quantum yield, indicating that the radiative rate constant $(k_r = \phi_{\rm fl}/\tau)$ of the **PI** excited state is essentially constant within the dyads. This fact further confirms that only a weak electronic coupling exists between the components in the dyads. The lifetime data at 77 K (Table 1) indicate that in **7** and **12** the quenching is blocked, whereas it is greatly reduced compared to fluid solutions in **5** and **6**, as already suggested by steady state determinations (see above). This is typical for electron-transfer processes: in fact, whereas fluid solvents can stabilise the charge-separated state by reorientation of the solvent molecules, frozen solvents cannot do so, and this often prevents electron transfer from occurring because of the insufficient or even negative driving force for the reaction.^[16]

Further evidence supporting quenching of perylene bisimide luminescence by electron transfer caused by the α effect (see Scheme 5) is that a blocking of the lone pair of the nitrogen atom in the isoxazolidine ring in **5** by protonation with trifluoroacetic acid or complexation with the Lewis acid boron trifluoride etherate switches the strong



Scheme 5. Electronic ground and excited states of 5 and 12.

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fluorescence of the perylene chromophore on again. These results clearly exclude quenching by predissociation of the weak N–O bond, because the N–O bond strength is only slightly altered by protonation or complexation.

To gain indisputable proof of electron transfer and to acquire information on the properties of the resulting chargeseparated state (CS), transient absorbance experiments were performed. Model PI displays quite different end-of-pulse absorption spectra in the two solvents (Figure 5). In toluene, negative signals around 575 and 625 nm due to the lowest energy bands of the stimulated emission, and positive peaks at 690 and \approx 850 nm, are detected. The spectrum has formerly been assigned to the PI singlet excited state, ¹PI,^[8a] and a similar assignment is carried out for the spectrum obtained in dichloromethane, in which the stimulated luminescence bands appear at 570 and 620 nm, whereas a positive intense and sharp peak occurs at 710 nm accompanied by a broad shoulder around 850 nm. Both spectra evolve very slowly in the explored timescale (0-3.3 ns), in agreement with a lifetime of ≈ 4 ns for ¹**PI**, as derived from luminescence data (Table 1). The results of a picosecond time-re-

> solved experiment of solutions of the dyads in dichloromethane are illustrated in Figure 6 for a couple of cases. All dyads dichloromethane display in spectra identical to the one for ¹**PI** (Figure 5), but the decay is faster than in the model. In Table 2 are reported the lifetimes determined from transient absorption spectroscopy, which, in the case of dichloromethane are similar, within experimental uncertainty, to the lifetime derived from luminescence experiments reported in Table 1. This confirms that the species detected in solutions of the dyads in dichloromethane is the singlet excited state localised on PI, and that no further product is formed, as indicated by the recovery of the spectra to the baseline. The results obtained in toluene are illustrated in Figure 7. The end-of-pulse spectrum is essentially coincident with the spectrum of ¹**PI** reported in Figure 5, but at variance with the dichloromethane case; it displays a time evolution to a different spectral profile with maxima at 710, 800, and 960 nm, which is typical of the PI radical anion.^[8a,17] The evolution from the ¹PI to the



Figure 5. Absorption spectra registered at the end of a laser pulse (35 ps, 532 nm, 3 mJ) in solutions of **PI** in toluene (grey) and dichloromethane (black); A = 0.65 in both solvents.



Figure 6. Absorption spectra registered after excitation with a laser pulse (35 ps, 532 nm, 3 mJ) of the dyads in dichloromethane; A is 0.65. Dyad **6**: end-of-pulse spectrum (grey), 230 ps (dashed line), 430 ps (black line) delays; dyad **12**: end-of-pulse spectrum (grey), 460 ps (dashed line), 960 ps (black line) delays. The time profile at 710 nm and exponential fittings are displayed in the inset.

PI⁻ spectrum has different lifetimes depending on the dyad: very slow in 12 and rapid in 5 or 6. Transient absorption signals at 710 nm, the maximum of PI⁻, can be fitted by a double exponential with a rising and a decaying part (Table 2). The rising part represents the formation of the radical anion PI⁻ from the decay of the singlet excited state ¹**PI**, and is in fact in good agreement with the luminescence lifetime (Table 1), whereas the decay represents the decay of the radical anion PI⁻, that is, the decay of the charge-separated (CS) state. In the case of dyad 12, whereas the formation of CS could be followed in the time window conveniently explored by the picosecond experiment (Figure 7), the decay was too slow and could be better registered with a nanosecond laser flash photolysis apparatus. The end-ofpulse spectrum in an Ar-saturated solution of 12 in toluene is reported in Figure 8 with the time evolution of the species. The lifetimes of the CS state varied in the dyads in the range of 0.3 to 15 ns.

The CS state has a spectrum essentially coincident with that of the reduced acceptor **PI**⁻. Contribution to the CS spectrum of the oxidised acceptor **IA**⁺ is apparently insignificant. To identify the absorption features of the latter, a chemical oxidation with excess Br_2 was performed with solutions of **IA** in dichloromethane.^[18] The resulting spectrum displayed only the Br_2 band around 400 nm, and no other specific absorbance attributable to the oxidised **IA** in the spectral range 400–1000 nm could be observed.

Electrochemistry: As emerged from the transient absorption data, the presence of the CS state is clearly identified in toluene, whereas in dichloromethane no evidence of such formation was found. To get a better insight into the thermodynamics and kinetics of this process, an examination of the electrochemical properties of the components was performed. Cyclic voltammetry of the four IAs in dichloromethane showed similar quasi-reversible oxidation waves, with peak potentials ranging from 1.04 to 0.93 V vs. SCE. The voltammogram of IA6 is displayed in Figure 9 as an example. The standard oxidation potentials, evaluated as the average of the potential of the oxidation wave maximum and that of its reverse wave maximum, are reported in Table 3 both vs. SCE and vs. ferrocene/ferricinium (Fc/Fc⁺) internal reference.^[19] No reduction waves were observed up to -2 V vs. SCE. In order to refer the redox potentials of both component moieties to the same electrolyte, the well-

Table 2. Transient absorption kinetic parameters and derived rate constants for charge separation and charge recombination reactions at room temperature.

	Toluene			Dichloromethane				
	$\tau [\mathrm{ns}]^{[\mathrm{a}]}$	$\tau \ [ns]^{[b]}$	$k_{ m cs} \; [{ m s}^{-1}]^{[{ m c}]}$	$k_{ m cr} [{ m s}^{-1}]^{[{ m d}]}$	$\tau [\mathrm{ns}]^{[\mathrm{a}]}$	$\tau \ [ns]^{[b]}$	$k_{\rm cs}^{\rm [c]}$	$k_{ m cr}{}^{[d]}$
5	0.23	0.30	3.6×10^{9}	3.3×10^{9}	_	0.23	3.9×10^{9}	\geq 3.9 × 10 ⁹ 3.9 × 10 ⁹
6	0.25	0.65	3.7×10^{9}	1.5×10^{9}	-	0.25	3.8×10^{9}	$\geq 3.8 \times 10^{9}$
7	0.50	0.75	1.7×10^{9}	1.3×10^{9}	-	0.50	1.7×10^{9}	$\geq 1.7 \times 10^{9}$
12	2.0	15 ^[e]	2.2×10^{8}	6.7×10^{7}	-	1.2	6.5×10^{8}	$\geq \! 6.5 \! \times \! 10^8$

[a] Risetime detected at 710 nm. [b] Decay time detected at 710 nm. [c] Charge-separation rate constant, derived from the average of the fluorescence and transient absorbance lifetime, see text. [d] Charge recombination rate derived from the decay lifetime at 710 nm. [e] From nanosecond flash photolysis.

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Figure 7. Absorption spectra registered after excitation with a laser pulse (35 ps, 532 nm, 3 mJ) of the dyads in toluene; A in the range 0.6–0.8. Dyad **5**: end-of-pulse spectrum (grey), 160 ps (dashed line), 460 ps (black line) delays; dyad **6**: end-of-pulse spectrum (grey), 160 ps (dashed line), 460 ps (black line) delays; dyad **7**: end-of-pulse spectrum (grey), 460 ps (dashed line), 790 ps (black line) delays; dyad **12**: end-of-pulse spectrum (grey), 790 ps (dashed line), 1940 ps (black line) delays. The time profile at 710 nm and bi-exponential fittings are displayed in the inset.

known cyclic voltammetry of **PI** was carried out under the same conditions as for the **IAs**, and showed two reversible monoelectronic reduction waves with the maxima at -0.67 and -0.88 V vs. SCE, respectively (Figure 9). The standard reduction potentials, also shown in Table 3, are in good



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Figure 8. End-of-pulse absorption spectrum registered after excitation with a laser pulse (20 ns, 532 nm, 3 mJ) in Ar-saturated toluene solutions of dyad 12; A = 1. The time profile and exponential fitting (grey) measured at 710 nm are displayed in the inset.



Figure 9. Current density measured in a CV of 10^{-3} M IA6 (dashed line) and PI (black line) at 0.1 Vs^{-1} in dichloromethane 0.1 M (C₄H₉)₄NClO₄; CV of Fc/Fc⁺ (grey) is also reported as an internal potential reference.

Table 3. Redox potentials of 10^{-3} M IA and PI from CVs at $0.1 V s^{-1}$ in dichloromethane $0.1 M (C_4H_9)_4 NClO_4$.

	E° [V vs. SCE]	E° [V vs. Fc/Fc ⁺]
IA5 oxidation	+0.83	+0.35
IA6 oxidation	+0.87	+0.39
IA7 oxidation	+0.88	+0.40
IA12 oxidation	+0.84	+0.36
PI 1st reduction	-0.62	-1.10
PI 2nd reduction	-0.83	-1.31

agreement with the results of other authors using the same solvent^[20] or other aprotic solvents.^[17,21] The **IAs** were shown to be moderate electron donors; on the other hand **PI** was confirmed to be a good electron acceptor. These conclusions can be extended to the same components in the dyads, taking into account the very poor electronic coupling of the two components (see above).

Photoinduced processes: To help the discussion and interpretation of the present photochemical data in the dyads, a very schematic energy level diagram can be drawn, as shown in Figure 10. The singlet-excited-state energy level localised on the perylene bisimide unit is 2.3 eV (from Table 1), whereas the standard reduction potentials of Table 3 allow an estimation, after convenient corrections, of

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Figure 10. Schematic energy level diagram and photoinduced processes in toluene and dichloromethane.

the energy of the charge-separated state corresponding to the oxidation of the IA unit which acts as donor (D) and the reduction of the PI unit which acts as acceptor (A). Following the Weller approach,^[22,23] the energy for the CS state PI^--IA^+ can be calculated as 1.32 eV for 5, 1.36 eV for 6, 1.35 eV for 7, and 1.36 eV for 12 in dichloromethane; these values can be considered the same for all cases. In toluene, due to the destabilisation brought about by the apolar solvent, the CS state has a higher energy: 1.94 eV for 5, 1.95 eV for 6, 1.92 eV for 7, and 2.07 eV for 12. While the values for 5-7 are essentially identical, for 12 the energy of the CS state is significantly higher, and probably due to the poor coulombic interaction between the two distant partners in the apolar medium.^[23] This is in fact the dyad with the largest separation, 15.7 Å, between D and A units. The treatment used for the calculation of the CS energy levels might overestimate^[24] the corrections in apolar solvents, therefore the reported energy levels should be taken as approximations.

The observed phenomena can be explained with reference to the energy-level scheme of Figure 10. Upon excitation of the PI unit in the dyad the singlet excited state localised on the perylene bisimide unit ¹PI-IA can accept an electron (HOMO-HOMO electron transfer) from the IA unit, leading to a charge-separated state $\mathbf{PI}^{-}\!\!-\!\!\mathbf{IA^{+}}$ with a consequent quenching of the fluorescent state. The rate constant of the reaction, k_{cs} , can be calculated for the various dyads using the equation $k_{cs} = 1/\tau - 1/\tau_0$, in which τ and τ_0 represent the lifetime of the excited state in the dyad and in the model, respectively. An average of the luminescence lifetime and of the transient absorbance lifetime is used for the τ of ¹**PI** in the dyads, and the calculated k_{cs} values are reported in Table 2. Whereas there is a difference between the rates of charge separation in the different dyads, which react in the order $5 \approx 6 > 7 > 12$ in each solvent, a difference between the reactivity of the same dyad in the two solvents is clearly detectable only for the "long" dyad 12, for which an increase by a factor of about three from toluene to dichloromethane can be noticed. This is in agreement with a "normal" behaviour, within the Marcus theory,^[25] which states that a higher driving force leads to a faster reaction. The ΔG^0 for charge separation is in fact approximately -0.2 eV in toluene, and

about -0.95 eV in dichloromethane for dyad 12. In all other cases, for which ΔG^0 for the charge-separation reaction varies from ≈ -0.4 to ≈ -0.95 eV, there are no significant differences caused by the solvent. It is very likely in the latter cases that ΔG^0 is sufficient in both solvents to place the reaction in the so-called "activationless region", in which the effect of the driving force on the reaction rate is levelled off. The distinct differences which can be noticed within the series in each solvent have to be assigned to electronic factors, that is, the electronic coupling between the donor and the acceptor. This is, quite understandably, less in 12, in which two phenyl groups are interposed between the active units and results in a slowdown of the charge-separation reaction. The differences between 5 and 6 on one side and 7 (which is apparently less efficient in promoting the coupling) on the other might be due to the different substitution pattern of the IA unit in 7, which has a carboxylic ester group in the α -position and might have a consequence on the reorganisation energy.^[25] The changes are, however, not very important, and result in a rate in 7 that is about half that of **5** or **6**.

A large effect of solvent polarity can, at variance with the charge-separation reaction, be detected on the charge recombination rate, k_{cr} . Whereas in toluene the spectral features of the CS state are clearly detected and its formation can be resolved from its decay (Figure 7), leading to measurable CS lifetimes ranging from 300 ps to 15 ns, in dichloromethane the formation of the charge-separated state is slower than or of the same order as the decay, and does not allow the species to accumulate. Therefore, in the latter solvent only the singlet excited state ¹**PI-IA** can be detected, and after its decay by electron transfer no new species is left, because $k_{cs} \leq k_{cr}$. The different behaviour in the two solvents is due to the large difference in the ΔG^0 for the recombination reaction: about -2 eV in toluene compared to around -1.35 eV in dichloromethane. In the toluene case, recombination occurs in the so-called "inverted" region according to Marcus theory,^[25] in which reactions with higher driving forces are slowed down.

Conclusion

Aldehydes from perylenetetracarboxylic bisimides have been successfully transformed to *N*-phenyl nitrones being efficient building blocks for the synthesis of isoxazolidines by the 1,3-dipolar cycloaddition with olefins. The regio- and stereochemistry in the isoxazolidines is controlled by electronic and steric effects in the starting olefins. Labile nitrones can be prepared in situ from aldehydes and *N*-phenyl hydroxylamine, and can be trapped with olefins. The synthesis of **IAs**, new promising electron donors, based on the α effect has been described, in which the 1,3-cycloaddition is applied as an efficient synthetic method. **IAs** have been successfully connected to perylenebisimide to form highly stable dyads, which can lead to charge separation upon absorption of visible light. Compounds such as **12**, for which

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charge separation is achieved with yields > 50% and lifetimes in the order of 10^{-8} s, are of interest for light-driven charge separation in several applications related to the exploitation of light energy. These arrays can find applications in conventional semiconductor solar cells, plastic solar cells, dye-sensitised solar cells, artificial photosynthesis and/or any light-driven redox process.

Experimental Section

Synthesis: IR spectrometry: Perkin–Elmer 1420 Ratio Recording Infrared Spectrometer, FT 1000; UV/Vis spectrometry: Varian Cary 5000 and Bruins Omega 20; fluorescence spectrometry: Perkin–Elmer FS 3000 (totally corrected); NMR spectroscopy: Varian VNMRS 600 MHz; mass spectrometry: Finnigan MAT 95.

N-(1-Hexylheptyl)-N'-(4-N"-methylcarbaldimin-N"-oxidobenzyl)pery-

lene-3,4:9,10-tetracarboxylic bisimide (3): Comopund $2^{[12]}$ (1.10 g, 1.59 mmol), N-methylhydroxylamine hydrochloride (200 mg, 2.39 mmol), and NaHCO₃ (287 mg, 3.31 mmol) were dissolved in CH_2Cl_2 (50 mL). The resulting solution was treated with MgSO4 (400 mg), heated under reflux for 5 h, stirred at room temperature for 16 h, filtered and evaporated, and the residue was purified by column separation (silica gel, dichloromethane/methanol 30:1). Yield 830 mg (65%) red dye; $R_{\rm f}$ (silica gel, dichloromethane/methanol 25:1)=0.30; m.p.>300°C; ¹H NMR (600 MHz, CDCl₃, 25 °C): $\delta = 0.83$ (t, ${}^{3}J = 6.8$ Hz, 1 H), 1.24–1.40 (m, 16H; CH₂), 1.88–1.93 (m, 2H; β -CH₂), 2.24–2.30 (m, 2H; β -CH₂), 3.88 (s, 3H; CH₃), 5.16-5.21 (m, 1H; CH-N), 5.42 (s, 2H; CH₂-N), 7.33 (s, 1H; CH-N), 7.60 (d, ³*J*=7.1 Hz, 1 H), 8.17 (d, ³*J*=7.1 Hz, 1 H), 8.57–8.68 ppm (m, 8H; H_{pery}); ¹³C NMR (150 MHz, CDCl₃, 25 °C): $\delta = 14.3$, 22.8, 27.2, 29.4, 32.0, 32.6, 43.8, 55.1, 123.1, 123.4, 126.5, 126.6, 128.9, 129.2, 129.6, 129.7, 130.0, 130.2, 131.3, 131.8, 132.0, 134.4, 135.1, 139.6, 163.5 ppm; IR (ATR): $\tilde{\nu} = 2955.4$ (m), 2919.5 (s), 2854.0 (m), 1692.4 (s), 1647.1 (s), 1591.7 (s), 1574.5 (m), 1505.8 (w), 1465.8 (w), 1435.8 (m), 1402.5 (m), 1353.1 (m), 1337.1 (s), 1250.4 (m), 1171.9 (m), 1127.2 (w), 1109.4 (w), 1005.5 (w), 982.7 (w), 851.2 (w), 809.2 (s), 744.5 (m), 645.2 cm^{-1} (w). UV/ Vis (CHCl₃): λ_{max} (E_{rel}) = 529 (1.0), 492 (0.60), 463 nm (0.21). MS (DEI⁺/ 70 eV): m/z (%): 720 (7) $[M^+]$, 719 (14), 704 (17), 703 (38), 702 (24), 538 (15), 537 (19), 523 (22), 522 (64), 521 (100), 520 (21), 509 (14), 508 (21), 374 (14), 373 (26), 346 (18), 260 (10), 148 (13); elemental analysis calcd (%) for C46H45N3O5 (719.9): C 76.75, H 6.30, N 5.84; found: C 76.69, H 6.24, N 5.66.

$N\-(1-Hexylheptyl)\-N'\-(4-N''\-phenylcarbaldimine\-N''\-oxidobenzyl)pery-$

lene-3,4:9,10-tetracarboxylic bisimide (4): Compound $2^{[12]}$ (1.10 g, 1.59 mmol) and N-phenylhydroxylamine (200 mg, 1.83 mmol) were dissolved in CH2Cl2 (50 mL). The resulting solution was treated with MgSO₄ (400 mg), heated under reflux for 5 h, stirred at room temperature for 16 h, filtered and evaporated, and the residue was purified by column separation (silica gel, dichloromethane/methanol 30:1). Yield 1.15 g (93%) red dye; $R_{\rm f}$ (silica gel, dichloromethane/methanol 25:1) = 0.36; m.p. > 300 °C; ¹H NMR (600 MHz, CDCl₂, 25 °C): $\delta = 0.83$ (t, ³J = 6.8 Hz, 1 H), 1.24–1.40 (m, 16 H; CH₂), 1.88–1.93 (m, 2 H; β -CH₂), 2.24– 2.30 (m, 2H; β-CH₂), 5.16-5.21 (m, 1H; CH-N), 5.37 (s, 2H; CH₂-N), 7.43–7.46 (m, 3H; H_{aryl}), 7.66 (d, ${}^{3}J = 8.4$ Hz, 1H; H_{aryl}), 7.74 (d, ${}^{3}J =$ 6.7 Hz, 1H; H_{arvl}), 7.90 (s, 1H; CH-N), 8.24-8.36 ppm (m, 8H; H_{perv}); ¹³C NMR (150 MHz, CDCl₃, 25 °C): $\delta = 14.0$, 27.0, 29.2, 31.8, 32.4, 43.5, 54.9, 121.7, 122.7, 122.9, 123.3, 124.1, 125.9, 126.0, 129.0, 129.1, 129.2, 129.3, 129.3, 129.9, 130.1, 130.8, 131.2, 131.6, 133.8, 134.0, 134.4, 139.8, 149.0, 163.0, 163.3 ppm; IR (ATR): $\tilde{\nu}$ = 3066.9 (w), 2952.0 (m), 2923.4 (s), 2854.1 (m), 1691.8 (s), 1646.1 (s), 1592.0 (s), 1575.4 (m), 1504.9 (w), 1483.0 (w), 1457.9 (w), 1435.6 (w), 1402.6 (m), 1334.8 (s), 1249.0 (m), 1170.8 (m), 1125.9 (w), 1108.1 (w), 1069.6 (w), 1022.9 (w), 987.3 (w), 892.3 (w), 850.5 (w), 832.3 (w), 809.6 (m), 763.0 (w), 684.9 (w), 660.6 (w), 622.5 cm⁻¹ (w); UV/Vis (CHCl₃): λ_{max} (ε)=463 (19600), 492 (53400), 529 nm (84300); MS (EI⁺/70 eV): m/z (%): 782 (10) [M^+ +H], 767 (15), 766 (33), 690 (26), 584 (56), 583 (87), 509 (50), 508 (90), 374 (14), 346 (21), 285 (23), 284 (100), 210 (20), 209 (25), 208 (24); elemental analysis calcd (%) for $C_{40}H_{41}N_7O_4$ (683.8): C 70.26, H 6.04, N 14.34; found: C 69.96, H 5.89, N 14.15.

 $N\-(1-Hexylheptyl)\-N'-(4\-N''-methylcarbaldimine\-N''-oxidobiphenyl)pery$ lene-3,4:9,10-tetracarboxylic bisimide (11): Compound 10 (100 mg, 0.130 mmol) was dissolved in styrene (5 mL). The resulting solution was treated with N-methylhydroxylamine hydrochloride (109 mg, 1.30 mmol) and sodium hydrogencarbonate (109 mg, 1.30 mmol), heated to 85 °C (30 min, slight evolution of gas, precipitation of a red solid), collected by vacuum filtration, and purified by column separation (silica gel, dichloromethane/methanol 30:1; rapid elution of two by-products and the starting material and collection of the red main fraction). The solvent was evaporated and the residue was dissolved in the minimal amount of dichloromethane and precipitated with methanol, collected by vacuum filtration, and dried in air at room temperature. Yield 53 mg (51%) red solid; $R_{\rm f}$ (silica gel, dichloromethane/methanol 30:1)=0.14; m.p.> 300°C; ¹H NMR (600 MHz, CDCl₃, 25°C): $\delta = 0.82$ (t, ³ $J_{H,H} = 7.0$ Hz, 6H; CH₃), 1.22–1.36 (m, 16H; CH₂), 1.85–1.91 (m, 2H; β -CH₂), 2.22–2.29 (m, 2H; β -CH₂), 3.89 (s, 3H; CH₃), 5.16–5.21 (tt, ${}^{3}J_{H,H} = 5.9$ Hz, ${}^{3}J_{H,H} = 9.3$ Hz, 1H; α -CH), 5.42 (s, 2H; CH₂-N), 7.38 (s, 1H; CH=N), 7.54–7.61 (m, 8H; $\rm H_{arom}),~8.48{-}8.54~ppm~(m,~8H;~H_{perylene});~^{13}C~NMR~(150~MHz,~CDCl_{3},$ 25°C): $\delta = 14.0, 22.6, 27.0, 29.2, 29.9, 31.8, 32.4, 43.4, 54.9, 122.9, 123.0,$ 123.1, 123.2, 127.0, 127.2, 127.5, 127.6, 128.9, 129.3, 129.5, 129.6, 129.7, 129.7, 130.2, 131.6, 131.6, 134.1, 134.8, 134.9, 135.0, 135.2, 136.7, 137.4, 139.0, 139.5, 163.3, 163.4 ppm; IR (ATR): $\tilde{v} = 2953.0$ (m), 2924.3 (m), 2855.7 (m), 1691.8 (s), 1651.9 (s), 1592.9 (s), 1576.8 (m), 1507.4 (w), 1495.9 (w), 1456.9 (w), 1435.7 (m), 1403.5 (m), 1379.0 (w), 1333.6 (s), 1248.8 (m), 1218.2 (w), 1195.3 (w), 1169.2 (m), 1126.5 (m), 1106.7 (m), 1003.1 (w), 988.4 (w), 943.0 (w), 853.3 (m), 808.0 (s), 782.8 (m), 748.1 (s), 721.2 (m), 667.0 (w), 639.5 (m), 615.4 (m), 587.4 cm⁻¹ (m); UV/Vis (CHCl₃): λ_{max} (E_{rel}) = 463 (0.22), 492 (0.61), 529 nm (1.0); HRMS: m/z: calcd for $C_{52}H_{49}N_3O_5$ 795.369; found: 795.371; $\Delta = 2$ mmu.

N-(1-Hexylheptyl)-N'-4-(5-methyloxycarbonyl-5-methyl-2-phenylisoxazolidine-3-yl)benzylperylene-3,4:9,10-tetracarboxylic bisimide (6): Compound 4 (110 mg, 141 µmol) was disperged in methyl methacrylate (20 mL), heated at 60 °C for 3 h (complete dissolution), allowed to cool, evaporated in vacuo and purified by column separation (silica gel, CH₂Cl₂/MeOH 50:1). Yield 87 mg (70%). R_f (silica gel, CH₂Cl₂/methanol 50:1)=0.80; m.p. > 300 °C; ¹H NMR (600 MHz, CDCl₃, 25 °C): δ =0.82 $(t, {}^{3}J = 7.0 \text{ Hz}, 3\text{ H}; \text{ CH}_{3}), 1.19 - 1.38 \text{ (m, 16H; CH}_{2}), 1.61 \text{ (s, 3H; CH}_{3}),$ 1.85–1.91 (m, 2H; β -CH₂), 2.22–2.29 (m, 2H; β -CH₂), 2.27 (dd, ³J= 7.4 Hz, ${}^{2}J = 12.5$ Hz, 1 H), 3.31 (dd, ${}^{3}J = 8.9$ Hz, ${}^{2}J = 12.5$ Hz, 1 H), 3.55 (s, 3H; OCH₃), 5.16–5.21 (m, 1H; α -CH), 4.74 (dd, ${}^{3}J=7.4$ Hz, ${}^{3}J=8.9$ Hz, 1H), 5.39 (s, 2H; N-CH₂), 6.81–6.83 (m, 1H; H_{aryl}), 6.89–6.90 (m, 2H; H_{arvl}), 7.18–7.13 (m, 2H; H_{arvl}), 7.57 (d, ${}^{3}J=8.4$ Hz, 2H), 7.43 (d, ${}^{3}J=$ 8.4 Hz, 2 H), 8.53 (d, ${}^{3}J = 8.1$ Hz, 2 H; H_{perylene}), 8.56 (d, ${}^{3}J = 8.1$ Hz, 2 H; $H_{\text{perylene}}),\ 8.62\text{--}8.67\ \text{ppm}\ (m,\ 4\,\text{H};\ H_{\text{perylene}});\ ^{13}\text{C}\ \text{NMR}\ (150\ \text{MHz},\ \text{CDCl}_3,$ 25°C): $\delta = 14.0, 22.5, 26.9, 29.2, 29.7, 31.8, 32.4, 43.4, 43.4, 49.8, 52.3, 54.8,$ 69.4, 83.2, 114.5, 117.0, 121.4, 122.9, 123.2, 124.1, 126.3, 126.6, 128.4, 129.6, 131.0, 131.0, 131.6, 134.2, 134.9, 136.4, 140.8, 151.1, 163.4, 164.6, 173.4 ppm; IR (ATR): $\tilde{\nu}\!=\!2921$ (m), 2852 (m), 1737 (w), 1693 (s), 1654 (s), 1593 (s), 1577 (m), 1507 (w), 1486 (w), 1434 (w), 1403 (m), 1377 (w), 1332 (s), 1300 (w), 1248 (w), 1201 (w), 1170 (w), 1125 (w), 1101 (w), 1021 (w), 981 (w), 853 (w), 809 (m), 743 (w), 694 cm⁻¹ (w); UV/Vis (CHCl₃): λ_{max} (ε) = 459.1 (18600), 491.0 (51400), 527.4 nm (85800); MS (DEI⁺/ 70 eV): m/z (%): 690 (33) $[M^+]$, 508 (100) $[M^+-C_{13}H_{26}]$, 374 (14), $[M^+$ $-C_{21}H_{35}O_2$], 346 (19) [*M*⁺ $-C_{22}H_{34}NO_2$], 44 (15) [CH₂NO]; HRMS: *m/z* calcd for $C_{56}H_{55}N_3O_7$: 690.309; found: 690.308; $\Delta = 1 \text{ mmu}$; elemental analysis calcd (%) for C56H55N3O7 (882.1): C 76.25, H 6.09, N 4.76; found: C 75.88, H 6.38, N 4.59.

N-(1-Hexylheptyl)-*N*'-4-(5-phenyl-2-phenylisoxazolidine-3-yl)benzylperylene-3,4:9,10-tetracarboxylic bisimide (5): Compound 4 (120 mg, 153 µmol) was dissolved in styrene (10 mL), heated at 85 °C for 1 h, allowed to cool, evaporated in vacuo, and purified by column separation (silica gel, CH₂Cl₂/methanol 20:1, mixture of two diastereomers, de =77% by ¹H NMR spectroscopy). Yield 102 mg (75%); $R_{\rm f}$ (silica gel, CH₂Cl₂/methanol 20:1)=0.79; m.p. > 300 °C; major diastereomer: ¹H NMR (600 MHz, CDCl₃, 25 °C): $\delta = 0.82$ (t, ³*J*=7.0 Hz,3H; CH₃),

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1.19-1.38 (m, 16H; CH₂), 1.85-1.91 (m, 2H; β-CH₂), 2.22-2.29 (m, 2H; β -CH₂), 2.43 (ddd, ³J=7.9 Hz, ³J=10.3 Hz, ²J=12.2 Hz, 1H; CH₂), 3.14 (ddd, ${}^{3}J = 5.7$ Hz, ${}^{3}J = 7.9$ Hz, ${}^{2}J = 12.2$ Hz, 1 H; CH₂), 4.88 (t, ${}^{3}J = 7.9$ Hz, 1 H; CH), 5.14 (dd, ${}^{3}J = 5.7$ Hz, ${}^{3}J = 10.3$ Hz, 1 H; CH), 5.16–5.21 (m, 1 H; α-CH), 5.39 (d, 1H; N-CH₂), 5.42 (d, 1H; N-CH₂), 6.88-6.91 (m, 1H; H_{aryl}), 7.01 (d, ${}^{3}J = 1.0 \text{ Hz}$, 2H; H_{aryl}), 7.02 (d, ${}^{3}J = 1.0 \text{ Hz}$, 2H; H_{aryl}), 7.21 (d, ${}^{3}J=7.4$ Hz, 2H; H_{aryl}), 7.23 (d, ${}^{3}J=7.4$ Hz, 2H; H_{aryl}), 7.28–7.30 (m, 1 H; H_{aryl}), 7.32–7.35 (m, 2 H; H_{aryl}), 7.39–7.41 (m, 2 H; H_{aryl}), 7.52 (d, ${}^{3}J =$ 8.4 Hz, 2H; H_{arvl}), 7.61 (d, ${}^{3}J = 8.4$ Hz, 2H; H_{arvl}), 8.52–8.65 ppm (m, 8H; H_{nervlene}); minor diastereomer: ¹H NMR (600 MHz, CDCl₃, 25 °C): $\delta =$ 0.82 (t, ${}^{3}J = 7.0$ Hz, 3H; CH₃), 1.19–1.38 (m, 16H; CH₂), 1.85–1.91 (m, 2H; β -CH₂), 2.22–2.29 (m, 2H; β -CH₂), 2.61 (ddd, ${}^{3}J$ =4.5 Hz, ${}^{3}J$ =6.5 Hz, $^{2}J = 12.0$ Hz, 1 H; CH₂), 2.74 (td, $^{3}J = 9.1$ Hz, $^{2}J = 12.0$ Hz, 1 H; CH₂), 4.66 $(dd, {}^{3}J=4.5 Hz, {}^{3}J=9.1 Hz, 1 H; CH), 5.16-5.21 (m, 1 H; \alpha-CH), 5.31 (dd,$ ${}^{3}J = 6.5$ Hz, ${}^{3}J = 9.1$ Hz, 1H; CH), 5.39 (d, 1H; N-CH₂), 5.42 (d, 1H; N-CH₂), 6.88–6.91 (m, 1H; H_{aryl}), 6.96 (d, ${}^{3}J = 1.0$ Hz, 2H; H_{aryl}), 6.97 (d, ³*J*=1.0 Hz, 2H; H_{aryl}), 7.15 (d, ³*J*=7.4 Hz, 2H; H_{aryl}), 7.17 (d, ³*J*=7.4 Hz, 2H; Haryl), 7.28-7.30 (m, 1H; Haryl), 7.32-7.35 (m, 2H; Haryl), 7.39-7.41 (m, 2H; H_{aryl}), 7.52 (d, ${}^{3}J=8.4$ Hz, 2H; H_{aryl}), 7.61 (d, ${}^{3}J=8.4$ Hz, 2H; H_{aryl} , 8.52–8.65 ppm (m, 8H; $H_{perylene}$); ¹³C NMR (150 MHz, CDCl₃, 25°C): $\delta = 14.0, 22.6, 26.9, 29.2, 31.8, 32.4, 43.4, 47.2, 48.8, 54.8, 69.4, 71.4,$ 80.5, 113.9 ,115.8 ,122.9, 123.2, 126.5, 126.8, 128.5, 128.9, 129.6, 129.7, 131.0, 131.8, 134.2, 134.8, 136.2, 137.7, 142.4, 152.5, 163.4 ppm; IR (ATR): $\tilde{\nu} = 3604.9$ (w), 3036.7 (w), 2954.5 (m), 2924.2 (m), 2855.3 (m), 1691.5 (s), 1655.3 (s), 1593.0 (m), 1577.8 (s), 1508.3 (w), 1484.6 (w), 1436.1 (m), 1403.7 (s), 1351.8 (s), 1332.5 (s), 1300.6 (m), 1249.1 (s), 1251.8 (w), 1169.9 (m), 1127.1 (w), 1104.9 (w), 1082.7 (w), 1020.7 (w), 983.9 (w), 924.9 (w), 854.54 (w), 810.2 (s), 796.1 (w), 771.8 (m), 748.3 (s), 696.2 $\rm cm^{-1}$ (s); UV/ Vis (CHCl₃): λ_{max} (ϵ)=459 (18800), 491 (52100), 527 nm (85700); HRMS: m/z calcd for C₅₉H₅₆N₃O₅: 886.426; found: 886.430; $\Delta = 4$ mmu; elemental analysis calcd (%) for $C_{59}H_{55}N_3O_5{\cdot}H_2O$ (885.4): C 78.38, H 6.35, N 4.65; found: C 78.17, H 6.70, N 4.34.

N-(1-Hexylheptyl)-N'-4-(5-cyano-2-phenylisoxazolidine-3-yl)benzylperylene-3,4:9,10-tetracarboxylic bisimide (8) and N-(1-Hexylheptyl)-N'-4-(4cvano-2-phenyl-isoxazolidine-3-yl)benzylperylene-3.4:9.10-tetracarboxylic bisimide (9): Compound 4 (110 mg, 153 µmol) was disperged in acrylonitrile (50 mL), heated under reflux for 1 h, allowed to cool, evaporated in vacuo, and purified by column separation (silica gel, CH2Cl2/methanol 45:1, mixture of two diastereomers, de = 52 % by ¹H NMR spectroscopy). Yield 94 mg (73%); $R_{\rm f}$ (silica gel, CH₂Cl₂/methanol 20:1)=0.79; m.p.> 300 °C; major diastereomer: ¹H NMR (600 MHz, CDCl₃, 25 °C): $\delta = 0.82$ (t, ${}^{3}J = 7.0$ Hz, 3H; CH₃), 1.19–1.38 (m, 16H; CH₂), 1.85–1.91 (m, 2H; β -CH₂), 2.22–2.29 (m, 2H; β -CH₂), 2.47 (ddd, ${}^{3}J=3.9$ Hz, ${}^{3}J=5.9$ Hz, ${}^{2}J=$ 12.8 Hz, 1 H; CH₂), 3.15 (ddd, ${}^{3}J=3.9$ Hz, ${}^{3}J=9.0$ Hz, ${}^{2}J=12.8$ Hz, 1 H; CH₂), 4.47 (dd, ${}^{3}J = 5.9$ Hz, ${}^{3}J = 9.0$ Hz, 1H; CH), 4.95 (dd, ${}^{3}J = 3.9$ Hz, ${}^{3}J$ = 9.0 Hz, 1H; CH), 5.16–5.21 (m, 1H; α -CH), 5.41 (s, 2H; N-CH₂), 6.94–6.95 (m, 3H; H_{aryl}), 7.18–7.24 (m, 2H; H_{aryl}), 7.49 (d, ${}^{3}J$ =8.3 Hz, 2H; H_{arvl}), 7.61 (d, ${}^{3}J=8.3$ Hz, 2H; H_{arvl}), 8.55–8.66 ppm (m, 8H; H_{perylene}); minor diastereomer: ¹H NMR (600 MHz, CDCl₃, 25 °C): $\delta =$ 0.82 (t, ${}^{3}J = 7.0 \text{ Hz}$, 3H; CH₃), 1.19–1.38 (m, 16H; CH₂), 1.85–1.91 (m, 2H; β -CH₂), 2.22–2.29 (m, 2H; β -CH₂), 2.77 (ddd, ${}^{3}J = 6.1$ Hz, ${}^{3}J = 7.6$ Hz, $^{2}J = 12.5$ Hz, 1 H; CH₂), 2.98 (ddd, $^{3}J = 5.2$ Hz, $^{3}J = 7.6$ Hz, $^{2}J = 12.5$ Hz, 1 H; CH₂), 4.87 (dd, ${}^{3}J = 5.2$ Hz, ${}^{3}J = 7.6$ Hz, 1 H; CH), 4.95–4.97 (m, 1 H; CH), 5.16–5.21 (m, 1H; α -CH), 5.41 (s, 2H; N-CH₂), 6.94–6.95 (m, 3H; H_{aryl}), 7.18–7.24 (m, 2H; H_{aryl}), 7.49 (d, ³J=8.3 Hz, 2H; H_{aryl}), 7.61 (d, $^{3}J = 8.3$ Hz, 2H; H_{aryl}), 8.55–8.66 ppm (m, 8H; H_{perylene}); elemental analysis calcd (%) for $C_{54}H_{50}N_4O_5$ (834.4): C 77.67, H 6.04, N 6.71; found: C 77.30, H 5.89, N 6.31.

N-(1-Hexylheptyl)-*N*'-4-(4-methyloxycarbonyl-5-methyl-2-phenylisoxazolidine-3-yl)benzylperylene-3,4:9,10-tetracarboxylic bisimide (7): Compound 4 (120 mg, 0.15 mmol) was disperged in methyl crotonate (20 mL), heated at 65 °C for 6 h (reflux), evaporated in vacuo, purified by column separation (silica gel, dichloromethane/methanol 50:1, non-fluorescent fraction), dissolved in a minimal amount of chloroform, and precipitated with methanol. Yield 80 mg (62.6%), bright red solid; $R_{\rm f}$ (silica gel, dichloromethane/methanol 30:1)=0.82; m.p. > 300 °C; ¹H NMR (600 MHz, CDCl₃, 25 °C): δ =0.82 (t, ³J(H,H)=7.0 Hz, 6H; 2×CH₃), 1.23–1.30 (m, 16H; 8×CH₂), 1.46 (d, ³J(H,H)=5.9 Hz, 3H; CH₃), 1.81–1.88 (m, 2H; β-CH₂), 2.21–2.27 (m, 2H; β-CH₂), 3.12 (dd, ³J(H,H)=7.1 Hz, ³J(H,H)= 9.2 Hz, 1H; CH), 4.38 (qd, ${}^{3}J(H,H) = 5.9$ Hz, ${}^{3}J(H,H) = 9.2$ Hz, 1H; CH), 5.10 (d, ${}^{3}J(H,H) = 7.1$ Hz, 1H; CH), 5.15–5.22 (m, 1H; α -CH₂), 7.19–7.22 (m, 5H; CH_{Aromal}), 7.53 (dd, ${}^{3}J(H,H) = 6.2$ Hz, 4H; CH_{Aromal}), 8.63– 8.73 ppm (m, 8H; CH_{Perylene}); 13 C NMR (151 MHz, CDCl₃, 25 °C): $\delta =$ 14.3, 22.8, 27.1, 29.4, 29.9, 32.0, 32.6, 55.0, 122.4, 123.8, 126.7, 129.1, 129.8, 131.9, 135.2, 136.7, 163.7 ppm; IR (ATR): $\bar{\nu} = 2935.4$ (w), 2923.6 (m), 2853.9 (m), 1736.0 (w), 1693.4 (s), 1654 (s), 1592.7 (s), 1577.5 (m), 1507.3 (w), 1486.1 (w), 1434.1 (m), 1403.2 (m), 1376.9 (w), 1331.6 (s), 1247.3 (m), 1216.2 (w), 1169.3 (w), 1124.5 (w), 1105.0 (w), 1020.8 (w), 987.5 (w), 851.8 (w), 808.8 (m), 744.0 (m), 694.4 cm⁻¹ (w); UV/Vis (CHCl₃): λ_{max} (ϵ) = 459 (21500), 490 (52400), 527 nm (84700); HRMS: m/z calcd for C₅₆H₅₆N₃O₅: 882.408; found: 882.409; $\Delta = 1$ mmu; elemental analysis calcd (%) for C₅₆H₅₅N₃O₅ (882.1): C 76.25, H 6.28, N 4.76; found: C 75.84, H 6.16, N 4.58.

N-(1-Hexylheptyl)-N'-4-(5-phenyl-2-phenylisoxazolidine-3-yl)biphenyl-

methyl-perylene-3,4:9,10-tetracarboxylic bisimide (12): Compound 10 (100 mg, 0.130 mmol) was dissolved in styrene (5 mL). The resulting solution was treated with N-phenyl hydroxylamine (142 mg, 1.30 mmol), stirred at 85°C for 25 h and then stirred at room temperature for a further 40 h. The solution was then evaporated in vacuo and the resulting residue was dissolved in dichloromethane, added to silica on a column for separation and eluted with dichloromethane/methanol 70:1 (first, non-fluorescent fraction). The first fraction was dissolved in the minimal amount of dichloromethane, precipitated with methanol, collected by vacuum filtration, and dried in air at 110°C (two diastereomers, de= 28% by ¹H NMR). Yield 34 mg (27%) red solid; $R_{\rm f}$ (silica gel, chloroform/ethanol=60:1)=0.28; m.p.> 300 °C; major diastereomer: ¹H NMR (600 Hz, CDCl₃, 25 °C): $\delta = 0.82$ (t, ${}^{3}J_{H,H} = 7.0$ Hz, 6H; CH₃), 1.21–1.36 (m, 16H; CH₂), 1.84-1.90 (m, 2H; β-CH₂), 2.20-2.28 (m, 2H; β-CH₂), 2.50 (ddd, ${}^{3}J_{H,H} = 7.7$ Hz, ${}^{3}J_{H,H} = 10.2$ Hz, ${}^{2}J_{H,H} = 12.2$ Hz, 1H; CH₂), 3.20 (ddd, ${}^{3}J_{HH} = 5.8 \text{ Hz}$, ${}^{3}J_{HH} = 8.0 \text{ Hz}$, ${}^{2}J_{HH} = 12.2 \text{ Hz}$, 1 H; CH₂), 4.95 (dd, ${}^{3}J_{H,H}$ = 7.8 Hz, 1 H; CH), 5.16–5.21 (m, 2 H; α -CH, CH), 5.46 (s, 2 H; CH₂-N), 6.93-7.72 (m, 18H; H_{arom}), 8.63-8.73 ppm (m, 8H; H_{perylene}); minor diastereomer (36%): ¹H NMR (600 Hz, CDCl₃, 25°C): $\delta = 0.82$ (t, ³J_{HH}= 7.0 Hz, 6H; CH_3), 1.21–1.36 (m, 16 , CH_2), 1.84–1.90 (m, 2 , $\beta\text{-CH}_2),$ 2.20–2.28 (m, 2 , β -CH₂), 2.69 (ddd, ${}^{3}J_{H,H}$ =4.6 Hz, ${}^{3}J_{H,H}$ =6.6 Hz, ${}^{2}J_{H,H}$ = 12.0, 1H; CH), 2.78–2.83 (m, 1H; CH), 4.72 (dd, ${}^{3}J_{H,H}$ =4.6 Hz, ${}^{3}J_{H,H}$ = 6.6 Hz, 1H; CH), 5.16-5.21(m, 1H; α-CH), 5.34-5.39 (m, 1H; CH), 5.46 (s, 2H; CH₂-N), 6.93–7.72 (m, 18H; H_{arom}), 8.63–8.73 ppm (m, 8H; $H_{perylene}$); ¹³C NMR (150 MHz, CDCl₃, 25 °C): $\delta = 14.0$, 22.6, 26.9, 29.2, 29.7, 31.8, 32.4, 43.5, 48.7, 54.8, 71.5, 80.8, 114.0, 121.4, 123.0, 126.7, 126.9, 127.2, 127.5, 128.6, 129.0, 129.5, 131.8, 135.0, 136.1, 137.8, 139.9, 140.2, 142.0, 152.5, 163.5 ppm; IR (ATR): $\tilde{v} = 3066.9$ (w), 2952.0 (m), 2923.4 (m), 2854.1 (m), 1691.8 (s), 1646.1 (s), 1592.0 (s), 1575.4 (m), 1483.0 (w), 1457.9 (w), 1435.6 (w), 1402.6 (m), 1334.8 (s), 1249.0 (m), 1170.8 (m), 1125.9 (w), 1108.1 (w), 1069.6 (w), 1022.9 (w), 987.3 (w), 892.3 (w), 850.5 (w), 832.3 (w), 809.6 (m), 763.0 (w), 684.9 (w), 660.6 (w), 622.5 cm⁻¹ (w); UV/Vis (CHCl₃): λ_{max} (E_{rel})=459 (0.21), 490 (0.60), 527 nm (1.0); HRMS: m/z calcd for C₆₅H₆₀N₃O₅: 962.456; found: 962.459; $\Delta = 3$ mmu. 4-(1,3-Dioxolane-2-yl)-4-methylbenzonitrile:^[26] 4-Cyano acetophenon (5.0 g, 34.4 mmol) was dissolved in toluene (50 mL). The resulting mix-

(5.0 g, 34.4 mmol) was dissolved in toluene (50 mL). The resulting mixture was treated dropwise with ethylene glycol (3.4 g, 55.1 mmol) and BF₃ etherate (0.5 mL), heated under reflux for 12 h at a water separator, allowed to cool at room temperature (yellow mixture), treated with 5% aqueous sodium hydrogen carbonate (40 mL), extracted with diethyl ether, washed with brine, dried with MgSO₄ and filtered. The filtrate was evaporated in vacuo and the residue crystallised from diethyl ether/*n*-pentane (1:1). Yield 2.2 g (34%) colourless solid; m.p. 70 °C; ¹H NMR (200 MHz, CDCl₃, 25 °C): $\delta = 1.62$ (s, 3H; CH₃), 3.72–3.75 (m, 2H; CH₂), 4.02–4.08 (m, 2H; CH₂), 7.57–7.64 ppm (m, 4H; H_{aryl}); HRMS: *m/z* calcd for C₁₁H₁₂NO₂: 190.086; found: 190.087; $\Delta = 1$ mmu.

4-(1,3-Dioxolane-2-yl)-4-methylbenzylamine: $[^{26]}$ 4-(1,3-Dioxolane-2-yl)-4-methylbenzonitrile (2.00 g, 10.6 mmol) in diethyl ether (10 mL) was added cautiously dropwise at 0°C under argon to a dispersion of lithium aluminium hydride (800 mg, 21.1 mmol) in diethyl ether (20 mL) over a period of 15 min. The resulting mixture was stirred at 0°C for 2 h and then at room temperature for a further 16 h; it was then hydrolysed by cautiously adding dropwise aqueous NaOH (2 N, 20 mL), extracted with

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diethyl ether (3×50 mL), dried with MgSO₄, filtered, and evaporated in vacuo. Yield 1.32 g (64%) colourless liquid; $n_D^{20}=1.552$; ¹H NMR (200 MHz, CDCl₃, 25°C): $\delta = 1.63$ (s, 3 H; CH₃), 3.72–3.75 (m, 2 H; CH₂), 3.84 (s, 2 H; N-CH₂) 4.02–4.08 (m, 2 H; CH₂), 7.26 (d, ³*J*=8.3 Hz, 2 H; H_{aryl}) 7.43 ppm (d, ³*J*=8.3 Hz, 2 H; H_{aryl}); MS (DEI⁺/70 eV): *m/z* (%): 193 (5) [*M*⁺], 178 (100), 134 (39), 87 (20), 43 (11).

N-[4-(2-Methyl[1,3]dioxolane-2-yl)benzyl]-N'-(1-hexylheptyl)perylene-

3,4:9,10-tetracarboxylic bisimide: N-1-Hexylheptylperylene-1,3:9,10-tetracarboxylic-3,4-anhydride-9,10-carboxylic imide (270 mg, 0.47 mmol) and imidazole (5 g) were heated at 140 °C and then treated with 4-(1,3-dioxolane-2-yl)-4-methylbenzylamine (110 mg, 0.56 mmol). The resulting mixture was stirred at 140 °C for 3 h and while still warm was treated with a few millilitres of ethanol and 2 N aqueous HCl (50 mL). The solution was then allowed to cool completely to room temperature and the precipitate was collected by vacuum filtration, washed with aqueous $2 \ {\mbox{\tiny N}}$ HCl and dried in air at 110°C for 16 h. It was then dissolved in the minimal amount of chloroform, and purified by column separation (silica gel CHCl₃/EtOH 30:1). Yield 246 mg (70%) red dye; R_f (silica gel, chloroform/ethanol 30:1)=0.17; m.p.>300 °C; ¹H NMR (600 MHz, CDCl₃, 25°C): $\delta = 8.43 - 8.57$ (m, 8H; H_{perv}), 7.54 (d, ${}^{3}J = 8.5$ Hz, 1H), 7.44 (d, ${}^{3}J =$ 8.5 Hz, 1H), 5.37 (s, 2H; CH₂-N), 5.16-5.21 (m, 1H; CH-N), 3.72-3.76 (m, 2H; CH₂), 3.98-4.00 (m, 2H; CH₂), 2.23-2.29 (m, 2H; β-CH₂), 1.86-1.92 (m, 2H; β -CH₂), 1.21–1.38 (m, 16H; CH₂), 0.82 ppm (t, ${}^{3}J$ =7.0 Hz, 1 H); ¹³C NMR (150 MHz, CDCl₃, 25 °C): $\delta = 163.2$, 142.7, 136.6, 134.7, 131.7, 131.6, 129.4, 129.3, 129.1, 129.0, 128.6, 125.5, 123.1, 22.9, 122.9, 108.7, 64.4, 54.8, 43.4, 32.4, 31.8, 29.2, 27.6, 27.0, 22.6, 14.0 ppm; IR (ATR): $\tilde{\nu} = 2955.0$ (m), 2923.9 (m), 2856.0 (m), 1693.1 (m), 1648.4 (s), 1592.9 (m), 1576.5 (m), 1507.5 (w), 1482.9 (w), 1456.8 (w), 1435.9 (m), 1420.5 (w), 1403.7 (m), 1378.5 (w), 1339.3 (m), 1284.2 (m), 1249.1 (m), 1173.2 (m), 1135.5 (w), 1127.9 (w), 1111.1 (w), 1091.7 (w), 1038.2 (m), 1020.2 (w), 983.8 (w), 948.3 (w), 862.4 (w), 808.9 (m), 781.1 (w), 744.4 (m), 725.4 cm⁻¹ (w); UV/Vis (CHCl₃): λ_{max} (ϵ) = 463 (81220), 492 (50320), 529 nm (18510); fluorescence (CHCl₃): λ_{max} (I_{rel}) = 539 (1.00), 582 nm (0.40); fluorescence quantum yield (CHCl₃, λ_{exc} =491 nm, $E_{491 \text{ nm}} = 0.0347 \text{ cm}^{-1}$, reference: **PI** with $\Phi = 1.00$): 1.00; MS (DEI⁺/ 70 eV): m/z (%): 749 (21) $[M^++H]$, 748 $[M^+]$ (38), 735 (13), 734 (47), 733 (100), 569 (12), 568 (18), 567 (21), 554 (11), 553 (34), 552 (41), 551 (43), 549 (13), 548 (31), 373 (11), 276 (12), 275 (30); elemental analysis calcd (%) for $C_{48}H_{48}N_2O_6$ (748.9): C 76.98, H 6.46, N 3.74; found: C 77.05, H 6.41, N 3.58.

N-(4-Acetylbenzyl)-N'-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic

bisimide: N-[4-(2-Methyl[1,3]dioxolane-2-yl)benzyl]-N'-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic bisimide (1.72 g, 2.30 mmol) was dissolved for deprotection in THF (220 mL) at 70 °C, treated with aqueous 2 N HCl (50 mL), heated at 70 °C for 5 h, and precipitated by the addition of 2 N HCl. The solid was collected by vacuum filtration, washed with distilled water, and dried at 110°C. Yield 1.60 g (98%) red dye; $R_{\rm f}$ (silica gel, chloroform/ethanol 30:1)=0.83; m.p. >300 °C; 1 H NMR (600 Hz, CDCl₃, 25°C): $\delta = 0.82$ (t, ${}^{3}J_{H,H} = 7.1$ Hz, 6H; CH₃), 1.19–1.39 (m, 16H; CH₂), 1.85–1.91 (m, 2H; β-CH₂), 2.22–2.28 (m, 2H; β-CH₂), 5.18 (tt, ${}^{3}J_{\text{H,H}} = 5.8 \text{ Hz}, {}^{3}J_{\text{H,H}} = 9.3 \text{ Hz}, 1 \text{ H}; \alpha\text{-CH}), 5.44 \text{ (s, 2 H; CH}_{2}\text{-N}), 7.77 \text{ (d,}$ ${}^{3}J_{\text{H,H}} = 8.5 \text{ Hz}, {}^{4}J_{\text{H,H}} = 173.9 \text{ Hz}, 4 \text{ H}; \text{ H}_{\text{arom}}), 8.55 - 8.65 \text{ ppm}$ (m, 8 H; $H_{perylene}$); ¹³C NMR (150 MHz, CDCl₃, 25 °C): $\delta = 14.0$, 22.6, 26.6, 27.0, 29.2, 29.7, 31.8, 32.4, 43.5, 54.9, 122.8, 123.0, 123.3, 126.3, 126.5, 128.6, 129.0, 129.5, 131.7, 134.1, 135.0, 136.4, 142.7, 163.3 ppm; IR (ATR): $\tilde{\nu} =$ 2957.0 (m), 2922.1 (m), 2855.1 (m), 1696.8 (m), 1674.8 (m), 1647.9 (s), 1608.3 (w), 1592.9 (m), 1576.1 (m), 1507.7 (w), 1482.9 (w), 1466.3 (w), 1436.6 (m), 1403.7 (m), 1379.4 (w), 1336.4 (s), 1310.1 (m), 1251.0 (m), 1192.4 (w), 1171.6 (m), 1124.9 (w), 1114.6 (w), 1076.7 (w), 1019.5 (w), 988.5 (m), 956.4 (w), 852.2 (w), 839.8 (m), 808.9 (s), 796.4 (m), 783.5 (m), 745.6 (s), 727.9 (w), 683.9 cm⁻¹ (w); UV/Vis (CHCl₃): λ_{max} (ϵ)=462 (20570), 491 (51780), 527 nm (84530); fluorescence (CHCl₃): λ_{max} (I_{rel}) = 539 (1.00), 582 nm (0.40); fluorescence quantum yield (CHCl₃, λ_{exc} = 491 nm, $E_{491 \text{ nm}} = 0.0294 \text{ cm}^{-1}$, reference: **PI** with $\Phi = 1.00$): 1.00; MS $(DEI^+/70 \text{ eV}): m/z \ (\%): 705 \ [M^+ + H] \ (24), 704 \ [M^+] \ (37), 524 \ (24), 523$ (76), 522 (100), 508 (11), 507 (24), 390 $[M^+-C_{13}H_{27}-C_9H_9O]$ (7), 374 (15), 373 (9), 346 (12), 254 (11), 55 (8); HRMS: m/z: calcd for $C_{46}H_{44}N_2O_5$: 704.327; found: 704.330; $\Delta = 3 \text{ mmu}$; elemental analysis

calcd (%) for $C_{46}H_{44}N_2O_5$ (704.3): C 78.38, H 6.29, N 3.97; found: C 77.96, H 6.21, N 3.91.

Spectroscopy and photophysics: Spectrophotometric grade toluene and dichloromethane (C. Erba) were used as supplied. A Perkin-Elmer Lambda 950 UV/Vis spectrophotometer was used to measure absorption spectra in 10 mm cells. A Spex Fluorolog II spectrofluorimeter was used to acquire fluorescence spectra in standard 10 mm fluorescence cells. Experiments at 77 K made use of capillary tubes dipped in a homemade quartz dewar filled with liquid nitrogen. Due to the geometrical conditions at 77 K, the absolute quantum yield cannot be determined with confidence, and only qualitative information can be derived. Solutions were air-equilibrated unless otherwise specified. The reported luminescence spectra are uncorrected; emission quantum yields were determined after correction for the photomultiplier response, with reference to an air-equilibrated solution of **PI** in dichloromethane with a $\Phi_{fl} = 0.99$.^[5] Luminescence lifetimes in the nanosecond range were obtained with an IBH single-photon counting equipment with excitation at 465 nm from pulsed diode sources (resolution 0.3 ns). For determination of emission lifetimes in the picosecond range an apparatus based on a Nd:YAG laser (35 ps pulse duration, 532 nm, 1.5 mJ) and a Streak Camera were used. The resolution time after deconvolutions is 5 ps.[27] Transient absorbance in the picosecond range made use of a pump and probe system based on a Nd:YAG laser (Continuum PY62/10, 35 ps pulse, 532 nm, 3 mJ). Solutions with absorbance of ≈ 0.6 -0.8 at the exciting wavelength were used. More details on the apparatus can be found elsewhere.^[28] Laser flash photolysis in the nanosecond range was performed with a Nd:YAG laser (18 ns pulse, 532 nm, 3 mJ) and an apparatus previously described.^[29] The samples were bubbled with Ar for about 15 min and sealed in homemade 10 mm optical cells. Molecular dimensions were estimated after MM2 minimisation by CS Chem 3D Ultra 6.0 software.^[30] Estimated errors are 10% on exponential lifetimes or 20% for more complex kinetic models, 20% on quantum yields, 20% on molar absorption coefficients, and 0.5 nm on emission and absorption peaks.

Electrochemistry: Redox potentials were determined at room temperature on 10^{-3} m solutions of **IA** or **PI** in dichloromethane (C. Erba RPE, distilled over P₂O₅ and stored under Ar pressure) with 0.1 m (C₄H₉)₄NClO₄ (Fluka, puriss. crystallised from methanol and vacuum dried). After Ar bubbling, cyclic voltammetry was performed at scan rates within 0.01–0.2 Vs⁻¹, in a homemade three-compartment glass cell under Ar pressure, by using an AMEL electrochemical system model 5000. The working electrode was semi-spherical Pt (area 0.05 cm²), the auxiliary electrode was a Pt wire, and the reference electrode was an aqueous KCl saturated calomel electrode (SCE). The SCE electrode was separated from the working electrode compartment by a liquid bridge, containing the same solvent and support electrolyte, and a low porosity glass frit. The potential of SCE with the liquid junction to dichloromethane 0.1 mol L⁻¹ (C₄H₉)₄NClO₄ was -0.475 V vs. Fc/Fc⁺.^[19]

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