DOI: 10.1002/chem.201000677

Multichromophoric Phthalocyanine–(Perylenediimide)$_8$ Molecules: A Photophysical Study

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Abstract: We describe the synthesis of a series of phthalocyanine (Pc)–perylenediimide (PDI)$_8$ "octad" molecules, in which eight PDI moieties are attached to a Pc core through alkyl-chain linkers. There is clear spectroscopic evidence that these octads can exist as non-aggregated "monomers" or form aggregates along the Pc cores, depending on the type of Pc and the solvent medium. In the low dielectric constant solvents, into which the octads are soluble, photoexcitation of the PDI units leads to rapid energy transfer to the Pc centre, rather than a charge separation between moieties. In octad monomers, the Pc singlet excited-state decays within tens of ps, whereas the excitons are stabilised in the aggregated form of the molecules, typically with lifetimes in the order of 1–10 ns. By contrast, in an octad design in which π–π interactions are suppressed by the steric hindrance of a corona of incompatible glycol tails around the molecule, a more straightforward photophysical interaction of Förster energy transfer between the PDI moieties and Pc core may be inferred. We consider these molecules as prototypical multichromophoric aggregates, giving delocalised states with considerable flexibility of design.

Keywords: chromophores • energy transfer • intermolecular aggregation • perylenes • phthalocyanines

Introduction

Multichromophoric molecular architectures and arrays, such as "dyads" and highly ordered supramolecules, have attracted a considerable amount of scientific interest as potential systems for the harvesting of energy in pseudo-biological antennae and photovoltaic assemblies.[1–3] These systems have many analogies to photophysical processes found in nature, such as those involved with photosynthesis, far in advance of anything currently attainable in human engineering.[4] Several strategies have been employed to mimic these natural energy-transfer processes, including the formation of polymer blends,[5] chromophoric arrays linked by covalent bonds[6] or by the use of self-assembly.[7] In all of these systems, photoexcitation is followed by energy transfer from one molecule to another, whereas very few systems involve energy or electron transfer from one very strongly interacting chromophore to another within the same molecular unit. The work reported herein aims to address issues associated with the use of suitable light-absorbing chromophores in advanced supramolecular designs. In such cases, energy transfer and light harvesting may be effectively controlled by the relative orientation and interaction of the chromophoric moieties and it is possible to envisage the optimisation of charge extraction through a hierarchical molecular organisation.

Perylenediimides (PDI), phthalocyanines (Pc) and various analogues have been extensively used as discrete components in supramolecular optoelectronic applications, such as transistors[8] and photovoltaic cells.[9,10] Pcs are an attractive

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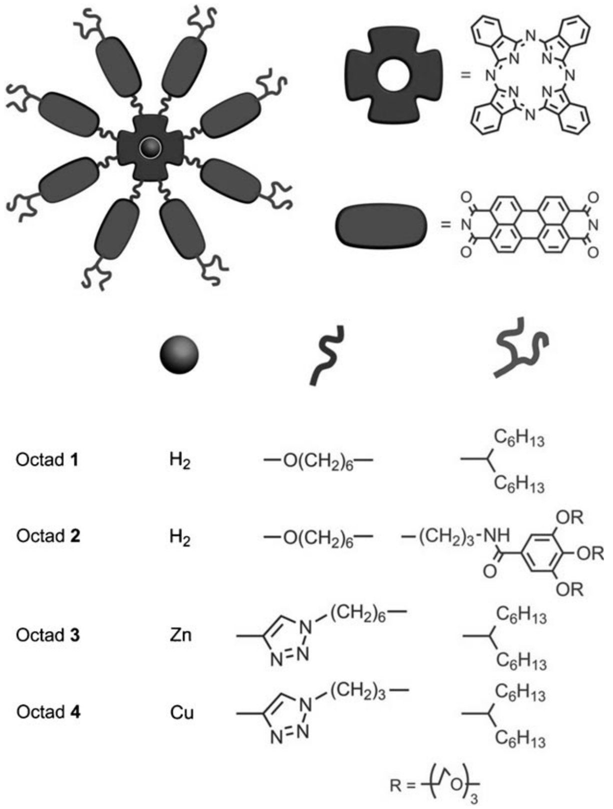
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201000677.

choice as they are known to have significant π–π interactions and readily form H aggregates.[11] In addition, they are closely related to the porphyrins seen in biological systems.[4] Herein, the synthesis of molecules with defined structures are reported; PDI and Pc units are built into the same macromolecular structure, with a high ratio of the sensitising component (PDI) relative to the Pc core. Eight individual PDI moieties are attached to a Pc core, through alkyl-chain linkers. We present a detailed photophysical study of four such "octad"[12] molecules within the context that these materials have the potential to be used as model systems for pseudo-biological light-harvesting antennae and photovoltaic assemblies.

The four molecules studied herein differ in terms of their peripheral substituents, the linking group between the Pc core and PDI units and whether metal ions are coordinated inside the Pc (Scheme 1). In the case of octad **1**, octad **3** and octad **4**, the perylene moieties are terminated with simple branched alkyl groups, whereas in octad **2**, these moieties are terminated with a bulky ethylene glycol side group. Octads **3** and **4** contain a metallated form of the Pc (Zn–Pc and Cu–Pc, respectively), whereas the free-base Pc moiety is used in octads **1** and **2**. Octad **4** has a shorter aliphatic linker group between the Pc and the PDI units, than those for the other structures. Octads **1**–**4** were synthesised by using highly modular approaches; in the final step of the synthesis, eight PDI moieties were coupled to a single Pc core by using either an efficient imide formation reaction (octads **1** and **2**) or by click chemistry[12,13] (octads **3** and **4**). The advantage of such modular approaches is the possibility to generate a wide range of products; the procedures allow for the preparation and the subsequent analysis of a library of materials with varying steric and electronic properties, provided that the final coupling step is highly efficient.



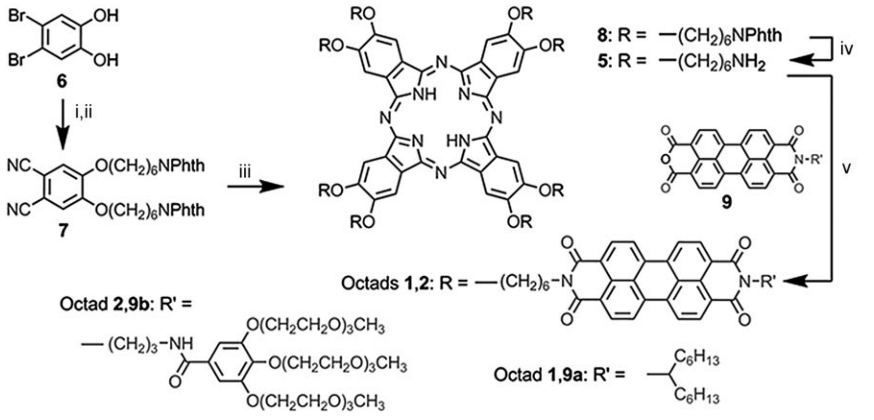
Scheme 1. Chemical structures of the four octad materials described in this paper. Octads **1** and **2** contain the free-base Pc as the core, whereas octads **3** and **4** contain Zn- and Cu-metallated Pcs respectively. Octads **1**–**3** contained C_6 alkyl-chain linkers between the core and 8 perylene (PDI) units, whereas octad **4** uses C_3 linkers. Octads **1**, **3** and **4** contained dialkyl side substitution of each of the PDI moieties, whereas octad **2** has much bulkier ethylene glycol substituents.

Our experiments illustrate how the photophysical properties may be altered by changes within the structure and the arrangement of the molecules. In particular, a correlation between intermolecular aggregation and the presence of long-lived excitations, as inferred from the ground-state bleach (GSB) lifetime, of the Pc core is observed. In solution, there is clear spectroscopic evidence that these octads can exist as monomers or form aggregates along the Pc cores, depending on the type of Pc and the solvent medium used. Transient absorption (TA) spectroscopy yields evidence of rapid energy transfer between π–π stacked PDI and Pc units for octads **1**, **3** and **4**, which is strongly favoured over charge separation, and which exceeds the calculated transfer rate for Förster resonant energy transfer (FRET). The singlet excited-state of Pc in octad monomers then shows an unusually fast decay, which is most likely to be caused by interaction with the PDI units, whereas in octads in which Pc aggregates are formed, the excitons are much longer lived (≈ns). We also find that intramolecular interactions between adjacent PDI units depend upon the tails of the PDI moieties. In octad **2**, however, in which such π–π interactions and intermolecular aggregation are suppressed by the steric hindrance of incompatible glycol tails around the molecule, a more straightforward process that involves FRET between the PDI moieties and the non-radiative Pc is observed. The much higher fluorescence quantum yield (QY) of octad **2**, relative to the other structures, is in good agreement with the much slower energy transfer to the Pc core in this case. The Zn–Pc(PDI)$_8$ system, octad **3**, (in toluene) shows a medium degree of aggregation; energy transfer to the Pc unit is followed by rapid decay of the Pc monomer excitons and the blueshifted Pc aggregate GSB is long-lived. The Cu–Pc(PDI)$_8$ system, octad **4**, shows the highest degree of stacking, even in solvents with a high solubility. Ultrafast energy transfer is followed by slow non-radiative decay of the Pc excitons, with $\tau \approx 8$ ns.

Results and Discussion

Synthesis: The synthetic approaches that lead to octads **1**–**4** were designed to proceed in a modular fashion; we focused on two highly efficient methods for the attachment of eight PDI units to the Pc core, which was prepared separately. Since the reaction comprises an eightfold coupling to one molecule, it is of key importance that this step proceeds with very high efficiency to avoid incomplete substitution and related purification issues.

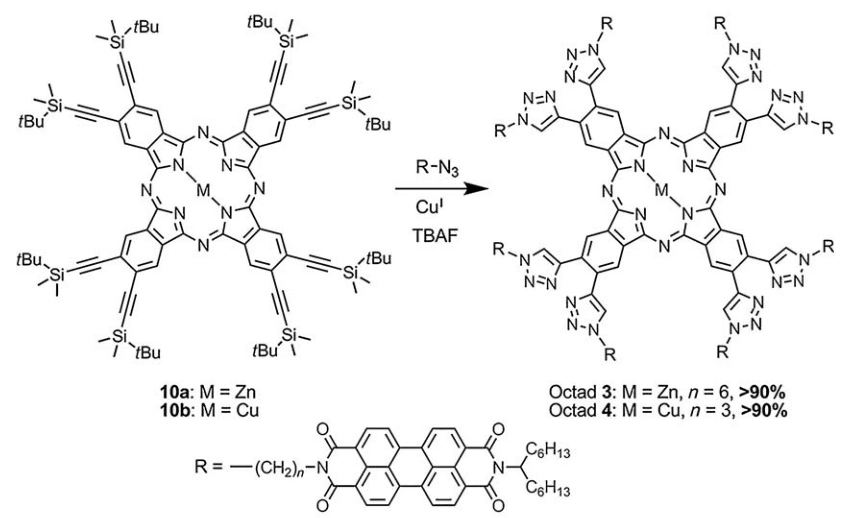
Two approaches were investigated: 1) attaching of the PDI moieties to the Pc core by use of a facile imide formation reaction (octads **1** and **2**) and 2) the cycloaddition of PDI azides to octaacetylene Pc by using click chemistry[13,14] (octads **3** and **4**). In the former approach, Pc **5**, equipped with eight amino groups, was used as the precursor (Scheme 2). The Pc was prepared in a three-step procedure from dibromocatechol (**6**) and a phthalimide-protected spacer (C$_6$) via intermediate **7**. The phthalimide protecting group was chosen for its stability in the Pc cyclisation reaction and its relatively mild, but high yielding, removal procedure with hydrazine. After chromatographic purification of Pc **8**, the amino groups were quantitatively deprotected with hydrazine hydrate in a mixture of ethanol and THF. The careful acid–base separation yielded the precursor **5** as the octa HCl salt (**5**•8HCl).



Scheme 2. Modular and efficient synthesis of octads **1** and **2** using octa amino- functionalised Pc **5** as the key precursor. i) Br(CH$_2$)$_6$NPhth (Phth = phthalimide, K$_2$CO$_3$, KI, butanone, 16 h, reflux, 87 %; ii) CuCN, DMF, 7 h, 130 °C, 67 %; iii) 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), C$_5$H$_{11}$OH, 16 h, 136 °C; iv) H$_2$NNH$_2$·H$_2$O, THF, EtOH, RT, quantitative; v) imidazole, pyridine, 4 h, 90 °C, 57–80 %.

Two different perylene monoanhydrides were attached to **5** to obtain octads **1** and **2**. Perylene **9a**[15] has a swallow tail, which introduces steric interactions and allows for the sufficient solubility of both the precursors and the final products.[16] Perylene **9b**[17] contains three oligoglycol tails attached to a short spacer to ensure excellent solubility in most organic solvents. We anticipated that the octads formed with **9b** would have a corona of incompatible glycol tails around the molecule, thereby aiding the formation of well-organised structures. For the synthesis of **9b**, gallic acid methyl ester was equipped with three glycol tails under straightforward etherification conditions. After saponification, a short propyl spacer with a terminal amino group was introduced. This water soluble precursor was selectively inserted onto one side of the perylene tetracarboxylic acid dianhydride by using the potassium salt route[18] (see the Supporting Information).

Octads **1** and **2** were prepared through an eightfold coupling of the perylene monoanhydride **9** to **5**•8HCl (Scheme 2). Since this is the key step in the procedure, the reaction conditions were optimised and it was found that a mixture of pyridine and imidazole at 90 °C gave superior results to the other systems tried. The reaction could be followed by means of MALDI-TOF spectrometry, which showed that the incompletely substituted oligomers disappeared after about 4 h. Subsequent precipitation and column chromatographic (SiO$_2$ and biobeads) separations yielded the product in excellent yields. This route provides an extremely high conversion reaction to couple PDI and Pc precursors.



Scheme 3. Modular and highly efficient in situ deprotection and clicking of PDI azides to the octa acetylene Pc **10** to generate octads **3** and **4**.

In the second approach (Scheme 3), a silyl-protected octaacetylene Pc **10** was used as the precursor. This molecule has proven to be a versatile building block in the synthesis of functionalised Pcs by the in situ deprotection and clicking with azides to give the desired products with quantitative conversions.[14] For this work, we have used the previously described protected Zn octaacetylene Pc **10a**[14] and the newly prepared copper analogue **10b**. Azide-functionalised PDIs with a short (C_3)[19] and a longer spacer (C_6)[20] were employed to obtain octads **3** and **4**.

Techniques for the structural characterisation of these compounds suffer from the strong stacking behaviour of the octads in most organic solvents. We found, however, that a combination of MALDI-TOF and GPC with a UV/Vis absorption detector at multiple wavelengths indicated a pure product in the case of octads **1** and **2**. As an example, the MALDI-TOF and GPC traces of octad **1** are shown in Figure 1. Mass analysis did not indicate the presence of six- or seven-fold substituted products.[21] Octads **3** and **4**, products of the cycloaddition reaction, were even harder to characterise because MALDI-TOF mass analysis resulted in substantial fragmentation of the compounds (loss of N_2 from the triazole ring and cleavage of the tails at the triazole ring).

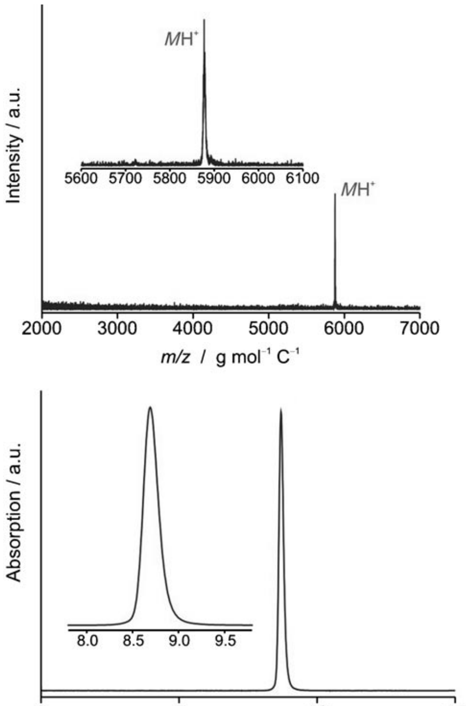


Figure 1. Top: MALDI-TOF spectrum (absorption at $\lambda = 520$ nm) of octad **1**. $M_{expl} = 5877.2$ g mol^{-1}, $M_{calcd} = 5876.9$ g mol^{-1}. Bottom: GPC trace of octad **1** (absorption at $\lambda = 520$ nm). The insets show a magnification of the corresponding spectrum. Characterisation data of octads **2**–**4** and the precursors are given in the Supporting Information.

Following thin-layer chromatography (TLC) measurements, which confirmed the purity and homogeneity of each of the four samples, cyclic voltammetry characterisation was performed on thin films of each of the octads; the key parameters are shown in Table 1. In addition to the determination of the potentials associated with the reduction of the PDI moieties and oxidation of the Pc cores, it was also possible to infer the electron affinity of the Pc as being the sum of the HOMO energy level and the optical-bandgap energy. The positions of the potentials (HOMO of Pc and LUMO of PDI) were all broadly in agreement with previously reported values.[22,23]

Table 1. Summary of key parameters derived from thin-film cyclic voltammetry data.[a]

	E_{red} [V]	E_{ox} [V]	LUMO (PDI) [eV]	HOMO (Pc) [eV]	LUMO (Pc)[b] [eV]
1	−0.80	+0.55	−4.00	−5.35	−3.65
2	−0.60	+0.6/0.7[c]	−4.20	−5.4/5.5	−3.7
3	−0.68	+0.62	−4.12	−5.42 (Zn–Pc)	−3.72
4	−0.67	+0.35	−4.13	−5.15 (Cu–Pc)	−3.45

[a] Measurements were taken at a scan rate of 20 mV s^{-1}, using a Pt working electrode, a Ag/AgCl reference electrode and acetonitrile as a solvent. The 1st oxidation (E_{ox}) and reduction (E_{red}) peaks are given relative to a ferrocene (Fe/Fe^+) standard at 4.8 eV. [b] The values of the Pc LUMO levels are inferred from the sum of the measured HOMO levels and the optical-bandgap energy. [c] The measured oxidation sweep for octad **2** was characterised by a very broad feature, with limited reversibility; an estimated value of E_{ox} is given, based on the oxidation onset.

Importantly, it is believed that the additional triazole groups in octads **3** and **4** do not have any significant effect on the electronic structure of the core. With two triazole groups in the *ortho* position in these octads, it would be sterically impossible for the triazole groups to be planar with the Pc core. Hence, conjugation is interrupted due to this deviation of the triazoles from the plane of Pc and it is likely, therefore, that only inductive effects through the sigma bonds are possible.

Photophysical characterisation: The absorption spectra for octads **1**–**4** in chloroform are shown in Figure 2; each octad showed a satisfactory solubility in this medium. In general, all materials show three distinct absorption peaks between

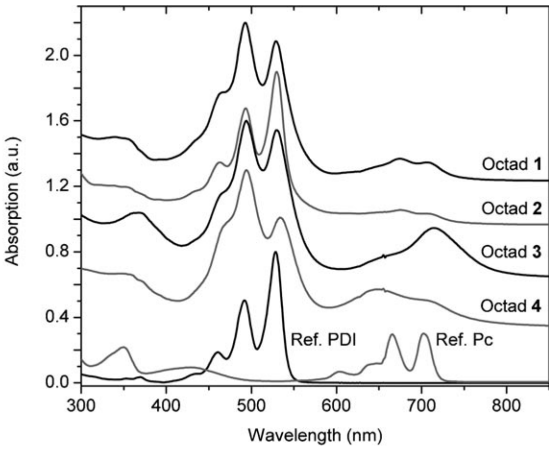


Figure 2. Absorption spectra of octads **1**–**4** in chloroform, as indicated, together with reference spectra of the free-base Pc and the monomeric form of the PDI moiety. In all cases, the samples were dispersed at a concentration level of around 100 µg mL^{-1}. The spectra are offset for clarity.

$\lambda = 450$ and 550 nm; this is characteristic of the S_0–S_1 transition of PDI. The broad features below $\lambda = 400$ nm are the Soret band and those beyond $\lambda = 600$ nm are the Q band of the central Pc unit. The comparison of these spectra with control samples of the PDI monomer and free-base Pc molecule in chloroform, however, revealed important differences. Only in the case of octad **2** does the spectrum appear to be a superposition of the PDI and Pc control spectra (noting that there are eight PDI units per Pc core), with the peaks displaying the same ratio of absorption oscillator strength as for the uncoupled chromophores. In the spectra for octads **1**, **3** and **4**, a significant redistribution of the oscillator strength in the fine structure of the PDI transition can be seen and is a consequence of electronic coupling of the PDI molecules with other conjugated species;[24] these may be other PDI units or the Pc core. There are also significant differences in the relative oscillator strengths of the fine structure of the Pc transitions, as well as an overall broadening, again indicating π–π coupling of the Pc core.

A comparison of the absorption and photoluminescence (PL) measurements in chloroform (good solvent) and in toluene (relatively poor solvent) for octad **1** is shown in Figure 3. The strongly blueshifted Q-band Pc absorption in toluene provides compelling evidence of intermolecular aggregation in this system.[6,7,25] Additional direct evidence of the presence of aggregates in solution is provided by dynamic light scattering (DLS) experiments, as shown in Supporting Information (Figure S2). Whilst octad **1** does not produce a DLS signal in chloroform due to a complete dissolution, in toluene the presence of intermolecular aggregates with a mean size of 15–20 nm is observed. The distribution of sizes by volume reveals a relatively broad variance in the mean size, with aggregates of >100 nm diameter being present. This behaviour is consistent with a stacked arrangement of the molecules, and a range of aggregate lengths.

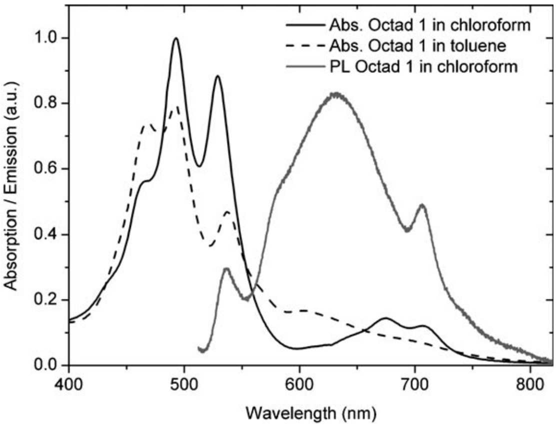


Figure 3. Solution absorption spectra of octad **1** in chloroform and toluene, together with the photoluminescence (PL) emission spectrum in chloroform. In all cases, the samples were dispersed at a concentration level of around 100 μg mL^{-1}.

The PL spectrum of octad **1** shows a significant redshifted emission, which is very characteristic of the presence of an aggregated state of the perylene units, which we would expect to have a relatively low QY.[26] To a lesser extent, this long-wavelength feature is also present in the PL spectra of octads **3** and **4**. By using the technique quantitative fluorimetry[27,28] in chloroform at room temperature, the fluorescence QYs were measured to be 11.2 % for octad **2**, whereas for octads **1**, **3** and **4** the values were found to be much lower (<1 %; Table 2). The measured QY value for the PDI monomer units in solution is 83 % and the QY values for PDI dimers from literature are of the order of 10 %. Such a large reduction in the QY of all octads is an initial indication of other competing, non-radiative pathways, which dominate over simple radiative recombination.[29]

Table 2. Key photophysical parameters of octads **1**–**4**, as derived from TA experiments in chloroform.

	PDI GSB lifetime [ps]	Pc GSB lifetime [ps][a]	Fitted energy-transfer time [ps]	Fluorescence QY [%][b]
1	2 (>95 %)	70	2–4	<1
2	1150	20	not visible	11.2
3	5	120	2–5	<1
4	1–2	8000[c]	1–2	<1

[a] $\lambda_{\mathrm{excitation}} = 650$ nm. [b] QY values below about 1 % are difficult to ascertain, because of low signal intensity. [c] Based on the fitting of the decay within the first 2 ns.

On account of the relatively high fluorescence efficiency of octad **2**, it was possible to probe the time dependence of PL by using time-correlated single-photon counting (TCSPC) measurements in dilute chloroform. The PL spectrum closely resembles that of the respective PDI monomer and is seen to decay mono-exponentially for all wavelengths, with a fitted lifetime of $\tau = 1.39$ ns. In solution, PDI units may exist either as unbound monomeric units, as dimers/aggregates with neighbouring units or they may form face-to-face dimers with the Pc core. The differences in behaviour are most likely to be due to the much greater steric hindrance of the peripheral substituents in octad **2**, relative to octads **1**, **3** and **4**, which will act to inhibit the stacking interactions between adjacent PDI units and the Pc core. In the case of octad **2**, we observed emission that is characteristic of PDI monomers, which is therefore attributed to uncoupled PDI units, with an efficient FRET process to the exposed Pc core. Taking into account the free-space PL lifetime of approximately 3.6 ns (rate, $k_{\mathrm{PL}} = 2.78 \times 10^8$ s^{-1}) and the expected energy-transfer rate from the model given in Figure S3 in the Supporting Information, which assumes a PDI–Pc spacing of 2.6 nm and random dipole orientation, the FRET rate is calculated to be $k_{\mathrm{ET}} = 1.21 \times 10^9$ s^{-1}. We can then predict how the QY of the emission will compare to the PDI monomer by using Equation (1):

$$\mathrm{QY}_{\mathrm{octad}} = \mathrm{QY}_{\mathrm{PDI}} \frac{k_{\mathrm{PL}}}{(k_{\mathrm{PL}} + k_{\mathrm{ET}})} \quad (1)$$

This approach gives an estimated QY for octad **2** of 15.4 %, which agrees with experimental results to within a 40 % margin of error, and a radiative lifetime ($1/\tau = k_{ET} + k_{PL}$) of 0.7 ns, which is in reasonably good agreement with experiments.

To gain a better qualitative insight into the photophysical properties of these octads and to probe the effects associated with the non-radiative Pc cores and the coupling between core and PDI units, TA spectroscopy enables us to monitor the dynamics of the excited states of the molecules on a timescale of hundreds of femtoseconds.[30] All the TA experimental results are summarised in Table 2.

In Figure 4, the TA spectrum for a range of delay times for octad **2** is shown. The positive signal at around $\lambda = 525$–600 nm has contributions from a GSB of PDI and also stimulated emission (SE). As is strongly consistent with the above analysis of radiative lifetimes, a GSB lifetime of 1150 ps is observed together with an intense photoinduced absorption band of the PDI exciton at $\lambda = 650$–750 nm, which decays on a similar timescale. Once FRET to the Pc has occurred, a rapid de-excitation within 20 ps occurs, as measured by TA when directly exciting the Pc core at $\lambda = 650$ nm. A similar relaxation process has been previously observed in comparable Pc chromophores and attributed to efficient nonradiative energy relaxation.[31] Such a process would also be consistent with the observed lack of Pc fluorescence. The results also suggest that the charge-separated state (Pc^+–PDI^-) is not strongly energetically favoured in these octads; indeed, no clear signs of the PDI anion are observed in the spectral regions where it would be expected to be visible.[32]

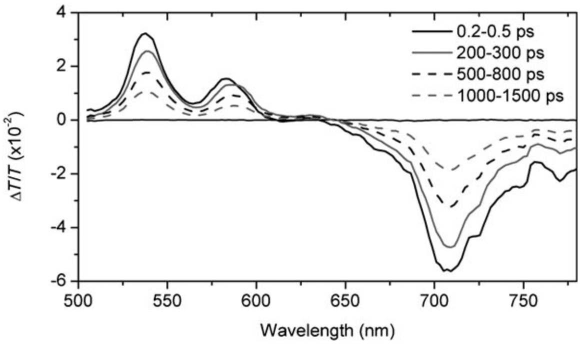


Figure 4. TA data for a solution of octad **2** (≈100 μg mL^{-1}) in chloroform for a range of probe-delay times up to 1500 ps, as indicated. The graph shows the fractional change in transmission ($\Delta T/T$) as a function of wavelength. Excitation was at $\lambda = 490$ nm.

The TA spectra for octads **1**, **3** and **4** in chloroform are shown in Figure 5 and display considerably more complex behaviour than is the case for octad **2**. Taking octad **1** as the paradigm (Figure 5, top left), we see the GSB of the PDI decays very rapidly on a timescale of 2 ps. Commensurately, we see a rise in the intensity of a new Pc GSB band at around $\lambda = 665$ nm, which then decays away over tens of ps. By exciting the sample at $\lambda = 650$ nm, we can directly excite the Pc core and measure the associated dynamics (Figure 5, top right). We measure the Pc GSB lifetime to be in the range of 70 ps. Notably, the TA spectra look qualitatively very similar if we compare the case of 50 ps after excitation at $\lambda = 500$ nm with the case of 2 ps after excitation at $\lambda = 650$ nm (Figure 6), which is compelling evidence of a very rapid energy-transfer process from PDI to Pc. Indeed, the rate of transfer exceeds the calculated rate for FRET, as described earlier.

A detailed analysis might require a quantum-chemical approach to determine the optimised geometries of the molecules, in both the un-aggregated and aggregated forms. However, the fitted PDI GSB lifetime of 2 ps may also be compared with the rate of energy transfer we might expect from the face-to-face stacking of PDI moieties with the Pc core. From the calculations presented in Figure S3 in the Supporting Information, assuming near-optimal arrange-

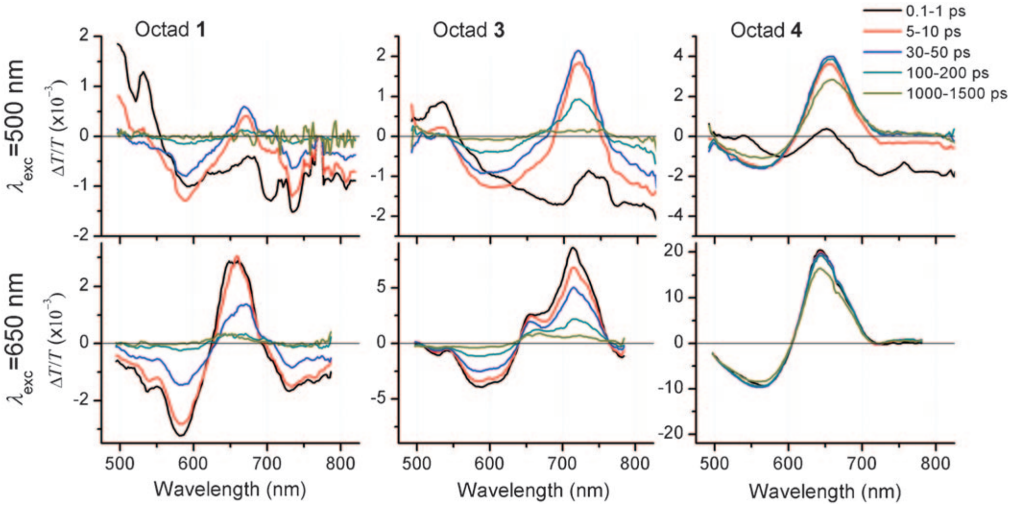


Figure 5. TA data for solutions of octads **1**, **3** and **4** (≈100 μg mL^{-1}) in chloroform for a range of probe-delay times, as indicated. The graphs show the fractional change in transmission ($\Delta T/T$) as a function of wavelength. Excitation was at $\lambda = 500$ nm or at $\lambda = 650$ nm, as indicated.

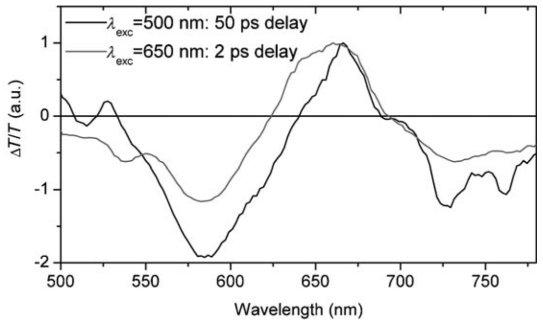


Figure 6. Qualitative comparison of the TA spectra for octad **1**, 50 ps after excitation at $\lambda = 500$ nm and 2 ps after excitation at $\lambda = 650$ nm. The spectra have been normalised for clarity.

ment of dipoles, it can be seen that a FRET rate of about 2 ps would correspond to a donor–acceptor spacing of around 1 nm, which is of the expected order for such molecular stacking. As a caveat, at such small spacings, the point-dipole assumption used in the FRET theory[33] is likely to become a poorer approximation,[34] especially as there is clear evidence of some delocalisation of states due to PDI–PDI dimer formation. It is noted that in another light-harvesting multichromophoric molecule based on PDI, reported by Rybtchinski et al., a similarly rapid FRET process was observed.[6]

The two octads with metallated Pc cores, showed TA behaviour that was broadly similar to that of octad **1** (Figure 5), despite the increased oscillator strength of the Pc absorption with respect to octads **1** and **2** and the shifting of the Q-band fine structure. In the case of octad **4**, however, the Pc GSB shows a greatly increased lifetime of 8 ns (Figure 5, bottom left/right). We note that, uniquely amongst these samples, octad **4** with the Cu–Pc shows spectroscopic evidence of strong intermolecular aggregation, even in solvent media in which the octads have a relatively high solubility, such as chloroform.

To investigate the correlation between the Pc GSB lifetime and the intermolecular aggregation in greater depth, further TA studies were carried out on octad **1**, allowing comparison of the behaviour in chloroform, toluene and in a solid-film (polystyrene) matrix (see Figure 7). It is clearly evident that the Pc GSB at around $\lambda = 650$ nm is very much longer-lived in the poor solvent toluene than in chloroform (Figure 5, top). Figure 7c shows how the signal intensity of the Pc GSB varies with pump-probe time delay in each case. In all cases, we observe a rapid rise time, associated with the transfer of excitons from the PDI halo to the Pc core. However, the GSB has a short lifetime in the order of tens of ps in chloroform, in which octad **1** is non-aggregated, but a much longer lifetime in the order of ns in toluene, in which aggregation is more strongly favoured. Also, the position of the Pc GSB in toluene is blueshifted compared with in chloroform, in agreement with the steady-state absorption spectra (c.f. Figure 3). The sample in polystyrene appears to show behaviour corresponding to an intermediate case of partial aggregation; presumably because the spin-coating method used to produce thin-films results in a metastable morphology, in which both intermolecular aggregates and non-aggregated forms of the octad are present. Consequently, the GSB shows a marked dynamic blueshift (Figure 7b), with the shorter- and longer-time spectra being characteristic of non-aggregates and aggregates, respectively.

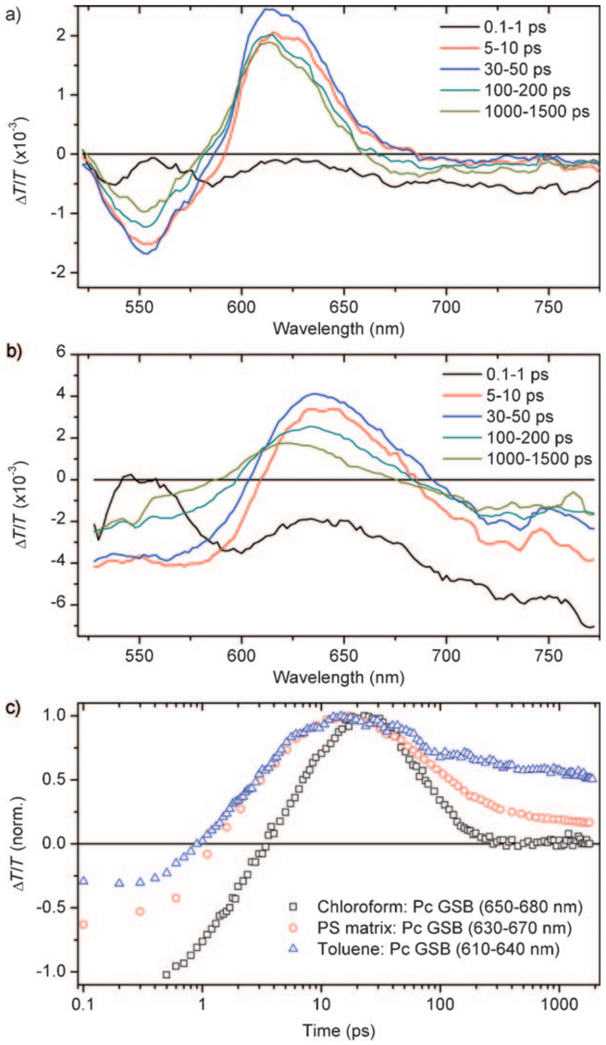


Figure 7. TA spectra for octad **1** ($\approx 100\ \mu g\,mL^{-1}$ a) in toluene and b) in a polystyrene (PS) matrix, corresponding to a range of probe-delay times, as indicated. The signal intensity of the Pc GSB is plotted as a function of time in (c), demonstrating how the Pc GSB decay lifetime is media dependent. Excitation was at $\lambda = 490$ nm and the spectra have been normalised for clarity.

Finally, some discussion regarding why energy transfer, and not charge separation, is the preferential pathway of relaxation in the octad molecules is warranted. Heterojunction blends of PDIs and metallated Pcs have previously been shown to be effective for use in photovoltaic cells, in which electron transfer onto the PDI component is energetically feasible.[35] Our observations of energy transfer and long-lived delocalised states are, however, more closely reminiscent of those reported for columnar aggregate structures of

Zn–Pc tetrakis(PDI) by Li et al.[7] In these molecules, and in the "octads" under consideration herein, there is no well-defined phase-separated heterojunction, across which charge separation may occur, as there is in a blend system. A pertinent comparison may be drawn with the work of Kim et al.,[36] who studied the photophysical differences between i) blend heterojunctions of two conjugated polymers and ii) analogous random co-polymers; observing the predominance of inter-chain charge separation in the former case, but rapid intra-chain energy transfer in the latter. Furthermore, in the low dielectric constant solvent media in which the octads are soluble, the critical distances for energy transfer (R_0) have large values of several nm,[37] implying that FRET processes are predominant over short-range Dexter-like charge tunnelling processes. Commensurately, it is likely that any charge separation between moieties will be unstable with respect to the excitonic states.

Conclusion

This paper describes the synthesis and photophysical characterisation of a series of Pc–PDI octad molecules in which eight perylene moieties are attached to a Pc core with alkyl-chain linkers. Our experiments illustrate how the photophysical properties may be altered by changes within the structure and the arrangement of the molecules; in particular, a correlation between intermolecular aggregation and the presence of long-lived excitations on the Pc core is observed. There is clear spectroscopic evidence, as well as direct physical evidence from DLS measurements, that these octads can exist as monomers or form aggregates along the Pc cores, depending on the type of Pc and the solvent medium used.

Photophysical characterisation illustrates how relaxation pathways may be altered by changes within the structure and the arrangement of the molecules. In the low dielectric constant solvents, in which the octads are soluble, photoexcitation of the PDI units leads to rapid energy transfer to the Pc centre, rather than a charge separation between moieties. In octad monomers, the Pc singlet excited-state decays within tens of ps, whereas the excitons are stabilised in the aggregated form of the molecules, typically with lifetimes in the order of 1–10 ns. By contrast, in an octad design in which π–π interactions and intermolecular aggregation are suppressed by the steric hindrance of a corona of incompatible glycol tails around the molecule, a more straightforward photophysical interaction of FRET between the PDI moieties and non-radiative Pc core is observed. The much higher fluorescence QY of this octad, relative to the other designs, is in good agreement with the reduced fluorescence lifetime of the PDI moieties in this case. In the case of an octad based on a metallated form of the Pc core, the Cu–Pc(PDI)$_8$ system, we find that aggregation and long-lived delocalised excitations are observed, even in solvents with a high solubility. Ultrafast energy transfer is followed by slow non-radiative decay of the Pc singlet excitons, with $\tau \approx 8$ ns.

Finally, these octad molecules demonstrate the ability to form the kinds of aggregated structures that may be conducive to the delocalisation of generated charges in the solid state. Whilst being beyond the scope of this present study, further work is also in progress to fully characterise the physical and photophysical properties in thin films. We anticipate the development of these materials as model systems of multichromophoric aggregates, exhibiting delocalised states. Adjustments to the rigidity of the linkers, which connect the various moieties, and to the arrangement and side substitution of the molecules may in the future enable the realisation of optimised hierarchical molecular structures, for pseudo-biological light-harvesting antennae.[6,38] In addition, further tuning of the energy levels of moieties might allow efficient charge generation and extraction along the stacks for use in solar cells.[39–42]

Experimental Section

For the TA experiments, solutions of the materials in chloroform ($\approx$10–100 μg mL^{-1}) were excited at $\lambda = 490$–500 or 650 nm by using the output of a commercial TOPAS (Light Conversion) pumped by an amplified Ti:sapphire laser system (Spectra-Physics Tsunami and Spitfire system) with a pulse duration of approximately 100 fs. More concentrated solutions were also studied, but no changes in kinetics were observed. The excitation power density was varied between 50 and 300 μJ cm^{-2} by using conventional neutral density filters. The TA behaviour was then probed with a white-light continuum, derived from a home-built, non-collinear optical parametric amplifier (NOPA) setup.[43] The NOPA generates an amplified white-light continuum in the range of $\lambda = 500$–800 nm. A fraction ($\approx$10 μJ) of the output of the regenerative amplifier is focused into a 2 mm thick sapphire plate for white-light seed generation, which is then amplified in a BBO crystal (cut at 32°) by overlapping with a focused 400 nm pump ($\approx$50 μJ) under a non-collinear angle, which allows for broadband phase matching. Only reflective optics are used to focus and collimate the white-light seed and the NOPA output to reduce the chirp of the white light. Both the 500 nm pump and the white-light probe are focused into the sample solution, which is held in a 1 mm thick quartz glass cuvette. Optimal spatial overlap is guaranteed by a significantly smaller probe beam spot. The probe beam arrival is varied in time, relative to the pump pulse, by the use of an optical-delay line.

Normal-incidence UV/Vis absorption measurements were made by using a Hewlett–Packard 8453 spectrophotometer. PL spectra were measured by using a calibrated fluorescence spectrophotometer (Cary Eclipse). Finally, time-resolved PL for octad **2** was measured, using a technique of time-correlated single photon counting (TCSPC). In brief, the samples were excited by using a $\lambda = 470$ nm ps pulsed diode-laser source, with the emitted photons being detected and binned based on their lag from the triggering pulse, with the limiting time-resolution of the experiment being around 100 ps. The PL lifetimes were then fitted by using linear regression curve-fitting software.

Acknowledgements

This work was supported by the ESF-SONS II-SUPRAMATES project and Marie Curie Research Training Network CHEXTAN (MRTN-CT-2004-512161). S.A.-S. thanks the Ernest Oppenheimer Foundations for funding. C.E.F. acknowledges the Leverhulme Trust (UK) for an Early Career Fellowship. F.L. thanks the Deutsche Forschungsgemeinschaft (DFG) for a postdoctoral research fellowship. P.H.J.K. thanks the EU (LC-energy) for financial support. A.E.R. thanks the Vidi and Vici. The authors thank Dr. G. Pace, F. Tian and Dr O. A. Scherman, of the University of Cambridge, for help with cyclic voltammetry and dynamic light scattering measurements.

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[20] See the Supporting Information: Experimental Section.

[21] Note: In our experience the presence of the free amino group in lower substituted octads ionises the molecule more readily, which makes it more visible in MALDI experiments. Their absence is a very strong indication that these materials are not present in the final product.

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Received: March 17, 2010