Intramolecular energy transfer in a tetra-coumarin perylene system: influence of solvent and bridging unit on electronic properties†

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The synthesis and characterisation of a novel coumarin donor–perylene bisimide acceptor light-harvesting system is reported, in which an energy-transfer efficiency of >99% is achieved. Comparison of the excited-state properties of the donor–acceptor system with model compounds revealed that although the photophysical properties of the perylene bisimide acceptor unit are affected considerably by the nature of the substituent at the imide positions and the solvent employed, through-bond interaction between the donor and acceptor units is negligible. Energy transfer in the present system can be described as occurring *via* a through-space energy-transfer mechanism. Careful consideration of the redox properties of the donor relative to the acceptor units allows for avoidance of potentially deleterious excited-state electron-transfer processes.

Introduction

Energy-transfer phenomena, such as those central to photosystems I and II,[1] and, in particular, in dye-based photovoltaic systems,[2] are of increasing importance in the drive to apply molecular systems as components in photonic devices and the ever increasing pressure to develop CO_2-neutral energy-generation technologies. Nature has served as a source of inspiration in understanding the basic requirements for building efficient energy-transfer systems,[1c,d] in particular in mimicking aspects of the complex architecture of the light-harvesting complexes PS I and PS II. In developing synthetic systems in which to study energy transfer but under low and high photon fluxes (so called multiphoton-excitation conditions) it is essential that the components employed are compatible energetically not only for efficient energy transfer but also to avoid potentially deleterious photochemistry, *e.g.* irreversible photoinduced electron transfer.[3]

Recently, we reported a tetra-coumarin–porphyrin-based dendritic system, which shows efficient intramolecular energy transfer.[4] However, the 7-methoxycoumarin-3-carboxylic acid selected for the tetra-coumarin–porphyrin system showed a decreased quantum yield of fluorescence when coupled to an amine, due to direct conjugation of the amide with the coumarin double bond. Furthermore, the porphyrin acceptor proved to be unstable under the intense irradiation conditions required to saturate the system.

Here, we report the design and photophysical characterisation of a coumarin donor–perylene bisimide acceptor system, which enables efficient light harvesting (Fig. 1). The perylene bisimide core is an excellent alternative for the porphyrin acceptor due to its high fluorescence quantum yield, redox properties, stability and the ability of perylene bisimides to engage in both electron- and energy-transfer processes.[5,6] These properties make them attractive for application in photonic devices and as substitutes for inorganic phosphorescent systems. Indeed, the similarity of both electronic and redox properties of perylene bisimides with the paradigm complex $[Ru(bpy)_3]^{2+}$ is remarkable.[7] The planarity of perylene bisimides enables the formation of H- and J-aggregates.[8] Such aggregation behaviour is advantageous for supramolecular systems,[9] in achieving gelation,[10] and in liquid-crystalline behaviour.[11] However, in studying unimolecular processes, such as energy and electron transfer in dendritic systems, aggregation is less desirable. In recent years, substitution in the bay area of the perylene bisimide has proven to be effective in inhibiting aggregation and as a consequence increasing solubility dramatically. Substitution in the bay area can be employed to connect the perylene bisimide unit to donor units also,[12] thereby combining increased solubility with increased functionality. In the present contribution substitution at the bay area is employed, as mentioned above, to facilitate solubility. Whilst other substituents, specifically energy-donor components, are introduced at the bisimide positions to provide the desired functionality.

The perylene bisimide core has been employed successfully in single- and multi-step donor–acceptor arrays, and has been shown to be a good acceptor with high stability as demonstrated by the groups of Fréchet,[13] Müllen,[14] De Schryver[14] and Würthner.[15]

The choice of donor unit is critical for the study of energy transfer in antenna systems, specifically Förster or resonance energy transfer. Importantly, the redox properties of the donor and the

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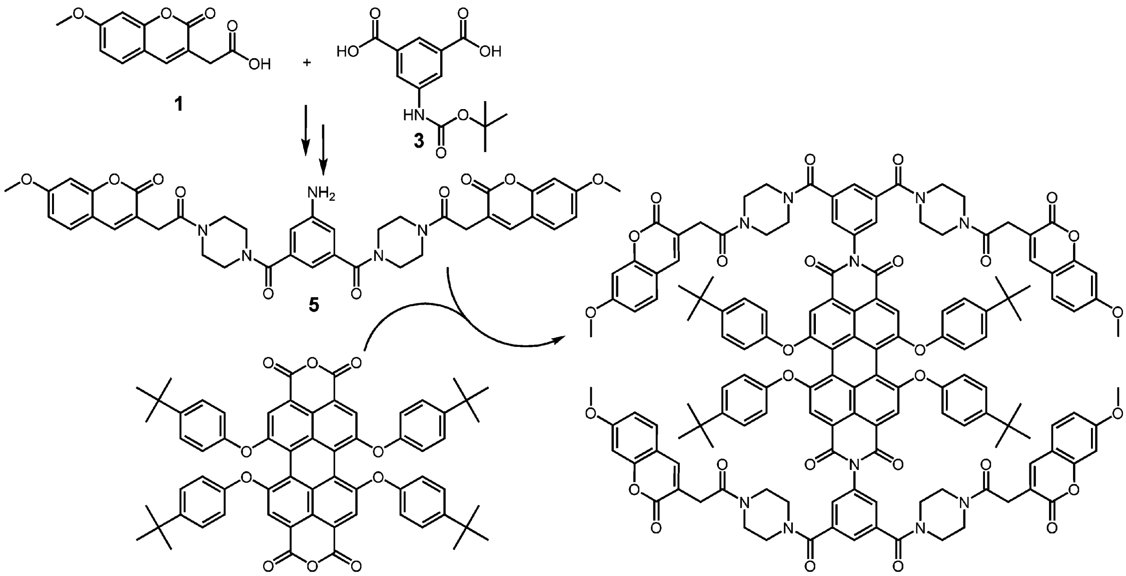

Fig. 1 Schematic representation of the convergent approach to the construction of the coumarin-perylene bisimide donor–acceptor system.

acceptor must not facilitate excited-state electron-transfer between donor and acceptor.[6c] To match these requirements, a highly fluorescent and stable, coumarin-based, donor was selected.[1b] The 7-methoxycoumarin-3-acetic acid **1** employed in this study was chosen to be compatible with the perylene bisimide core, in terms of both electronic and redox properties. Furthermore, the carboxylic acid functionality facilitates the use of amide chemistry.

A further important consideration lies in the properties of the bridging unit between the donor and acceptor components that enable reasonable control of the donor–acceptor separation and, to a lesser extent, orientation. Dendritic systems, *i.e.* large regularly branched molecules,[16] are of special interest as candidates in energy-transfer systems, as demonstrated by the groups of Balzani,[17] Fréchet[13] and Wasielewski.[5] Dendrimers offer a possibility of arranging donor and acceptor units and of controlling communication between these chromophores, and it is this covalent-tethering approach, which is taken in the present study. In the present study, which focuses on through-space energy transfer, the bridging unit should not allow through-bond energy-transfer processes to occur. Therefore, piperazine and amides were used as spacer groups to disrupt through-bond electronic communication between the donor and acceptor units.

The polarity of the amide bonds provides an opportunity to examine the effect of solvent polarity on the conformation of the dendritic structure and also its effect on the energy-transfer efficiency. In this paper we present the design and synthesis of an efficient donor–acceptor system (Fig. 1), together with a photophysical investigation of both the donor and acceptor components and of the assembled donor–acceptor system.

Experimental

Uvasol-grade solvents (Merck) were employed for all spectroscopic measurements. All reagents employed in synthetic procedures were of reagent grade or better, and used as received unless stated otherwise. *N*-Boc-piperazine,[18] 5-(*N*-Boc-amino)isophthalic acid,[19] **7**,[20b] **8**,[20c] and **9**[20d,e] were prepared according to literature procedures. Details of the experimental procedure for the synthesis of **10**, **12a** and **12b**, and of the measurements performed can be found in the ESI†.

3-Acetic acid-7-methoxycoumarin (1)

2-Hydroxy-4-methoxybenzaldehyde (25 g, 0.16 mol) and succinic anhydride (50 g, 0.50 mol) were placed in a 250 ml three-necked round-bottom flask fitted with a reflux condenser. The solid mixture was heated on a metal plate to 90 °C and stirred for 30 min. The melt was then heated to 190 °C. Anhydrous succinic acid, disodium salt (38 g, 0.23 mol) was added in small portions over 4 h. The hot melt was poured into 10% HCl (aq) and left overnight. The yellowish precipitate was filtered and washed with water until neutral. The residue was dissolved in 5% $NaHCO_3$ (aq) and filtered. The filtrate was added to cold 15% HCl (aq) and left overnight. The precipitate was filtered and the residue washed with H_2O, dried, and recrystallised from H_2O–ethanol yielding brownish crystals (8.28 g, 35.8 mmol) in 21,8% yield. m.p. 177.5–177.9 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$) $\delta = 12.47$ (s, 1H), 7.90 (s, 1H), 7.60 (d, $J = 8.6$ Hz, 1H), 7.01 (d, $J = 2.4$ Hz, 1H), 6.95 (dd, $J = 8.6, 2.5$ Hz, 1H), 3.85 (s, 3H), 3.45 (s, 2H). ^{13}C NMR (50 MHz, DMSO-d$_6$) $\delta = 171.41$ (s), 161.89 (s), 160.86 (s), 154.58 (s), 141.74 (d), 128.95 (d), 119.23 (s), 112.41 (d), 112.38 (s), 100.42 (d), 55.81 (q), 35.60 (t). MS(EI) for $C_{12}H_{10}O_5$ m/z 234 [M$^+$], HRMS calcd for $C_{12}H_{10}O$ 234.053, found 234.053.

7-Methoxy-3-(2-oxo-2-(*N*-Boc-piperazine)-1-yl-ethyl)coumarin (1a)

N,*N*′-Carbonyldiimidazole (CDI) (1.4 g, 8.5 mmol) was added to a suspension of 3-acetic acid-7-methoxycoumarin (2.0 g, 8.5 mmol) in dry CH_2Cl_2. The reaction mixture was stirred at room temperature (RT) under N_2 until CO_2 evolution was complete, and stirring was continued for another 30 min. *N*-Boc-piperazine (1.57 g, 8.5 mmol) was added and the reaction mixture was stirred under N_2 at RT overnight. The reaction mixture was extracted twice with 1 M HCl (aq), twice with 5% $NaHCO_3$ (aq), and once with brine. The solution was dried over Na_2SO_4 and the solvent evaporated. The crude mixture was purified using column chromatography (2% MeOH in CH_2Cl_2, SiO_2, $R_f = 0.4$) giving a yellow solid (3.13 g, 7.76 mmol) in 91.8% yield. m.p. 164.0–164.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.65$ (s, 1H), 7.32 (d, $J = 8.6$ Hz, 1H), 6.80 (dd, $J = 8.5$, 2.4 Hz, 1H), 6.78 (d, $J = 2.3$ Hz, 1H), 3.83 (s, 3H), 3.58 (dd, $J = 9.0$, 5.0 Hz, 4H), 3.56 (s, 2H), 3.48-3.42 (m, 2H), 3.42-3.37 (m, 2H), 1.43 (s, 9H). ^{13}C NMR (100.6 MHz, $CDCl_3$) $\delta = 168.4$ (s), 162.4 (s), 161.9 (s), 155.1 (s), 154.5 (s), 141.8 (d), 128.5 (d), 119.3 (s), 112.6 (s), 112.9 (d), 100.5 (d), 80.2 (s), 55.7 (q), 45.96 (t), 41.8 (t), 34.0 (t), 28.3 (q). MS(EI) for $C_{21}H_{26}N_2O_6$ m/z 402 [M$^+$], HRMS calcd for $C_{21}H_{26}N_2O_6$ 402.179, found 402.180.

General deprotection method for BOC-protected amines

The Boc-protected amine was stirred in a mixture of 1 : 1 CH_2Cl_2–CF_3COOH for 4 h. An equal amount of water was added and the mixture was neutralised by addition of solid $NaHCO_3$, after which the aqueous layer was separated and the organic layer was washed with saturated $NaHCO_3$ solution. Subsequently the organic layer was dried over Na_2SO_4 and the solvent evaporated. The resulting product was used in subsequent steps without further purification.

(3,5-Bis{4-[2-(7-methoxy-2-oxo-2*H*-chromen-3-yl)acetyl]piperazine-1-carbonyl}phenyl)carbamic acid *tert*-butyl ester (4)

BOC-protected 7-methoxy-3-(2-oxo-2-(*N*-Boc-piperazine)-1-yl-ethyl)coumarin (**1a**) was deprotected using the general method described above, and (2.0 g, 6.6 mmol) of the deprotected compound was suspended in THF with 5-(*N*-Boc-amino)isophthalic acid (0.66 g, 2.4 mmol). 4-(4,6-Dimethoxy-1,3,5-triazin-2-yI)-4-methylmorpholinium chloride (DMTMM) (2.0 g, 7.2 mmol) was added and the suspension was stirred overnight. The solvent was evaporated and the crude mixture was purified using column chromatography (4% MeOH in CH_2Cl_2, SiO_2, $R_f = 0.4$), yielding a light yellow solid (0.87 g, 1.02 mmol, 43%) m.p. 190.5–191.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.66$ (s, 2H), 7.53 (s, 2H), 7.34 (d, $J = 8.6$ Hz, 2H), 7.08 (s, 2H), 6.97 (s, 1H), 6.82 (dd, $J = 8.6$, 2.4 Hz, 2H), 6.79 (s, 2H), 3.84 (s, 6H), 3.81–3.36 (m, 20H), 1.49 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$) $\delta = 169.2$ (s), 168.5 (s), 162.4 (s), 161.9 (s), 155.1 (s), 152.5 (s), 142.0 (d), 139.6 (s), 136.2 (s), 128.5 (d), 119.6 (d), 119.2 (s), 118.3 (d), 112.8 (s), 112.7 (d), 100.4 (d), 80.9 (s), 55.7 (q), 47.5 (t), 46.0 (t), 41.9 (t), 34.1 (t), 28.2 (q). MALDI-TOF MS ($M_w = 849.32$) $m/z = 872.51$ [M + Na$^+$].

N,*N*′-(3,5-Bis{4-[2-(7-methoxy-2-oxo-2*H*-chromen-3-yl)acetyl]piperazine-1-carbonyl}phenyl)-1,6,7,12-tetrakis[4′-*tert*-butylphenoxy]-3,4:9,10-perylenetetracarboxylic diimide (12c)

In a 100 ml round-bottom flask fitted with a reflux condenser **10** (100 mg, 0.10 mmol), **5** (225 mg, 0.30 mmol) (obtained after deprotection of **4** *via* the standard procedure) and dimethylacetamide (20 ml) were heated and stirred at 120 °C under dinitrogen. After 5 days the reaction was judged complete (by TLC, 10% MeOH in CH_2Cl_2, SiO_2). The reaction mixture was poured into 50 ml 1 M HCl (aq) and left to stand overnight. The precipitate was filtered off and the residue washed with 1 M HCl (aq) and water. The residue was taken up into MeOH–CH_2Cl_2 1 : 1, dried over Na_2SO_4, and the solvent evaporated. The crude compound was purified by column chromatography (4% MeOH in CH_2Cl_2, SiO_2) yielding the purple product **12c** (40 mg, 0.016 mmol, 16%). ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 8.26$ (s, 4H), 7.65 (s, 4H), 7.63 (t, $J = 1.5$ Hz, 2H), 7.43 (d, $J = 1.3$ Hz, 4H), 7.35 (d, $J = 8.6$ Hz, 4H), 7.23 (d, $J = 8.9$ Hz, 8H), 6.85–6.77 (m, 16H), 3.86 (s, 12H), 3.83-3.38 (m, 40H), 1.26 (s, 36H). ^{13}C NMR (100.6 MHz, $CDCl_3$) $\delta = 169.5$ (s), 169.4 (s), 164.2 (s), 163.5 (s), 163.0 (s), 157.2 (s), 156.2 (s), 153.7 (s), 148.6 (s), 143.1 (d), 137.5 (s), 136.2 (s), 134.2 (s), 130.7 (d), 129.6 (d), 127.8 (d), 123.2 (s), 122.1 (s), 121.4 (d), 120.8 (s), 120.4 (s), 120.3 (d), 113.9 (d), 113.8 (d), 101.6 (d), 56.8 (q), 48.7 (d), 47.1 (d), 43.3 (d), 35.4 (d), 35.2 (d), 32.5 (q), 30.7 (s). MALDI-TOF MS ($M_w = 2447.91$) $m/z = 2470.46$ [M + Na$^+$].

(5-*tert*-Butoxycarbonylamino)isophthalic acid bis(2,5-dioxopyrrolidin-1-yl) ester (13)

A suspension of 5-(*N*-Boc-amino)isophthalic acid (1.0 g, 3.5 mmol) and *N*-hydroxysuccinimide (886 mg, 7.7 mmol) in dry THF under a dinitrogen atmosphere was stirred at 0 °C. *N*,*N*′-Dicyclohexylcarbodiimide (1.6 g, 7.7 mmol) was added, and the solution was stirred overnight at RT. The suspension was filtered and the filtrate collected. The solvent was evaporated and the resulting solid was recrystallised from 2-propanol yielding a white powder (853 mg, 1.77 mmol, 51%). m.p. 205.1–205.6. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 8.50$ (s, 1H), 8.44 (s, 1H), 6.99 (s, 2H), 2.90 (s, 8H), 1.52 (s, 9H). ^{13}C NMR (50.3 MHz, $CDCl_3$) $\delta = 169.1$ (s), 160.7 (s), 152.3 (s), 140.4 (s), 127.1 (s), 126.4 (d), 125.4 (d), 82.2 (s), 28.4 (q), 25.9 (t). MS(EI) for $C_{23}H_{33}N_3O_4$ m/z 475.1 [M$^+$].

[3,5-Bis(piperidine-1-carbonyl)phenyl]carbamic acid *tert*-butyl ester (14)

A suspension of **13** (2.0 g, 4.2 mmol), piperidine (1.1 g, 12,6 mmol) and triethylamine (1.3 g, 21.6 mmol) in CH_2Cl_2 (100 ml) was stirred overnight under a dinitrogen atmosphere. The suspension was subsequently washed with a 1 M HCl (aq) (twice), a saturated aqueous $NaHCO_3$ solution (twice), water and finally with brine. The organic layer was dried with Na_2SO_4, and the solvent evaporated. The solid residue was dissolved in MeOH, after which the product was precipitated by dropwise addition to 1 M HCl (aq). The white precipitate is filtered, washed with water and dried in a vacuum oven at 40 °C, yielding a white powder (1.18 g, mmol, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 9.66$ (s, 1H), 7.51 (s, 2H), 6.87 (s, 1H), 3.56 (s, 4H), 3.25 (s, 4H), 1.48 (s, 9H), 1.38–1.65 (m, 12H). ^{13}C NMR (50.3 MHz, $CDCl_3$) $\delta = 169.4$ (s), 152.8 (s), 139.7 (s), 137.5 (s), 119.0 (d), 118.0 (d), 80.9 (s), 49.0 (t), 43.4 (t), 28.5 (q), 26.7 (t), 25.8 (t), 24.7 (t). MS(EI) for $C_{23}H_{33}N_3O_4$ m/z 415 [M$^+$], HRMS calcd for $C_{12}H_{10}O$ 415.248, found 415.247.

Results and discussion

The construction of the donor–acceptor systems employs sequential amide-coupling steps in a convergent manner. The coumarin donor units were connected to branching unit **3** *via* two consecutive amide-coupling reactions (Fig. 2). First, the acetic acid-functionalised coumarin **1** was connected to a mono-Boc piperazine, after which the protecting group was removed to give the amine-functionalised coumarin **2**. The functionalised coumarin **2** was then coupled to 5-(*N*-Boc-amino)isophthalic acid using 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMTMM) with an overall yield of 20%, after which the protecting group was removed yielding **5** (Fig. 2), which was used without further purification.

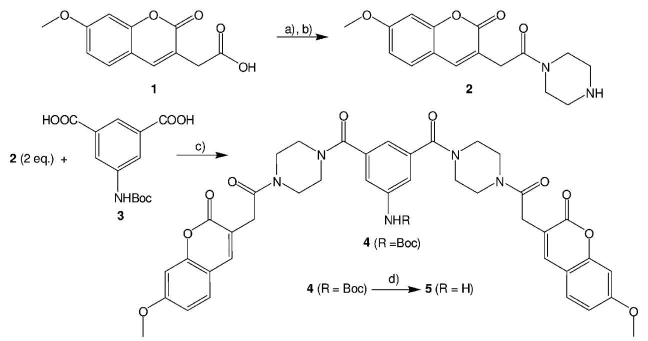

Fig. 2 Synthesis of the dicoumarin branch **5**: (a) CDI, CH_2Cl_2, *N*-Boc-piperazine; (b) CH_2Cl_2, CF_3COOH, 4 h; (c) DMTMM, THF, 18 h; (d) CH_2Cl_2, CF_3COOH, 4 h.

The core unit was prepared using literature procedures.[20] The perylene bisanhydride **6** was transformed to the *n*-butyl bisimide **7** by condensation with *n*-butylamine (Fig. 3). The bisimide was tetra-chlorinated using sulfuryl chloride in nitrobenzene to yield **8**. Aromatic substitution using 4-*tert*-butylphenol provided the tetraphenol-substituted perylene bisimide **9**. The bisimide was saponified with potassium hydroxide to give the tetra(4-*tert*-butylphenoxy)-substituted bisanhydride **10** after acidic work-up in 46% yield over 4 steps (Fig. 3).

Condensation of **10** with an excess of **5** provided, after purification, the tetra coumarin perylene bisimide **12c** in 16% yield. The model compounds **12a** and **12b** were synthesised following similar procedures (Fig. 4).

The compounds were purified by column chromatography and characterised by ^{1}H and ^{13}C NMR spectroscopy and MALDI-TOF mass spectroscopy (see experimental section for details).

Electronic properties

The absorption spectra of the perylene bisimide model compounds and **12c** in CH_2Cl_2 are shown in Fig. 5 and the data are summarised in Table 1. Examination of the spectra of the substituted perylene bisimides (Fig. 5) reveals a bathochromic shift with decreasing electron donating strength of the substituent. The visible absorption spectrum ($\lambda > 400$ nm) of **12b** is almost identical to that of **12c**. This indicates that the electronic influence of the substituent is limited to the bridging unit itself and any influence of the coumarin component observed is unlikely to be through bond in character.

Emission spectra ($\lambda_{ex} = 450$ nm) of the model compounds (Fig. 6) and **12c** show a trend analogous to that observed in the absorption spectra; a slight bathochromic shift is observed with decreasing electron-donating strength of the substituent (Table 1). As a consequence of the similarity of the redox (*vide infra*), absorption and emission properties of **12b** and **12c**, the former

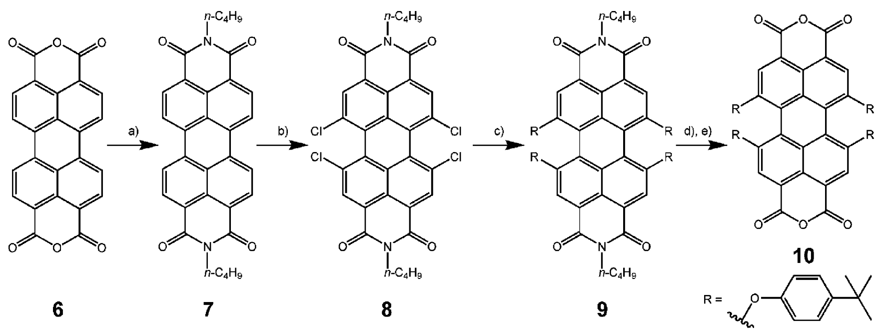

Fig. 3 Synthesis of the core acceptor unit (a) *n*-butylamine, quinoline, 220 °C, 6 h; (b) SO_2Cl_2, I_2, PhI, $PnNO_2$, reflux, 80 °C, 20 h; (c) 4-*tert*-butylphenol, K_2CO_3, NMP, 130 °C, 3 days; (d) KOH, H_2O, *t*-BuOH, reflux, 24 h; (e) HCl (aq).

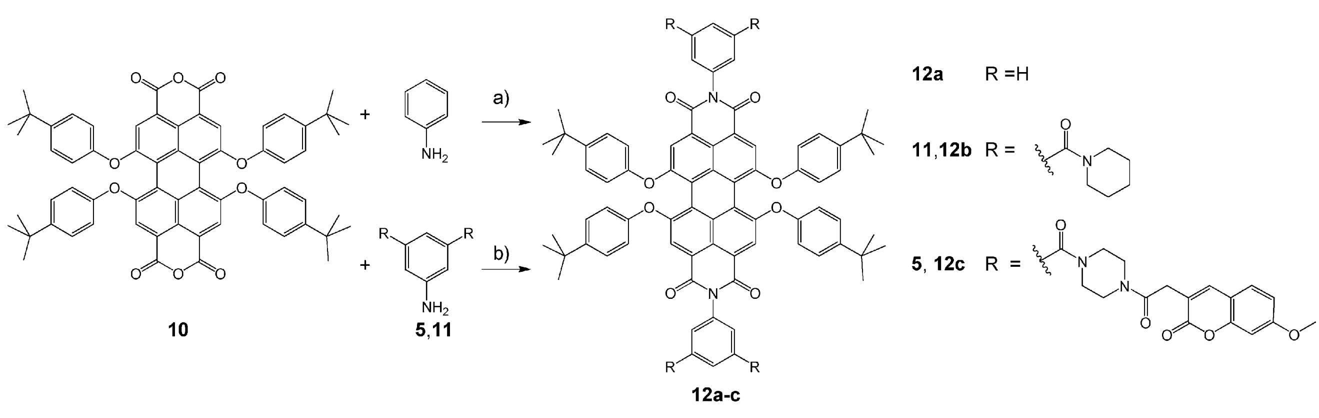

Fig. 4 Synthesis of **12a–c**: (a) toluene, 120 °C, 5 d; (b) DMA, 120 °C, 5 d.

Table 1 Absorption and emission spectra of **4**, **9** and **12a–c**[a]

	Absorption	Emission	Lifetime
	λ_{max}/nm (10^3 ε/cm^{-1} M^{-1})	λ_{max}/nm (Φ_{fl})	τ/ns^b
1a	322(18.3)	393^d (0.46^d)	1.38^d
4	324(31.3)	394^d (0.50^d)	1.51^d
9	266(40.6), 286(49.6), 451(16.7), 539(26.7), 577(43.1)	608^e (0.66^i)	6.66^f
12a	265(43.0), 290(43.6), 452(16.9), 540(28.1), 580(45.7)	612^e (0.59^i)	6.46^f
12b	289(41.9), 455(15.7), 544(28.1), 584(44.6)	616^e (0.57^i)	6.30^f
12c	295(63.6), 322(61.5), 458(14.5), 546(25.7), 587(41.9)	394^d, 618^d ($<0.03,^{d,g}$ $0.47^{h,i}$)	5.94^f
4 + **12c**^{c}	294, 321, 455, 544, 584	394^d, 619^d (n.d.)	n.d.

^{a} Recorded in CH_2Cl_2 at RT. ^{b} Emission lifetime, experimental uncertainty ~2.5%. ^{c} 2 : 1 mixture. ^{d} $\lambda_{ex} = 322$ nm. ^{e} $\lambda_{ex} = 450$ nm. ^{f} $\lambda_{ex} = 420$ nm. ^{g} Residual coumarin emission. ^{h} Direct excitation of the perylene bisimide unit. ^{i} $\lambda_{ex} = 539$ nm.

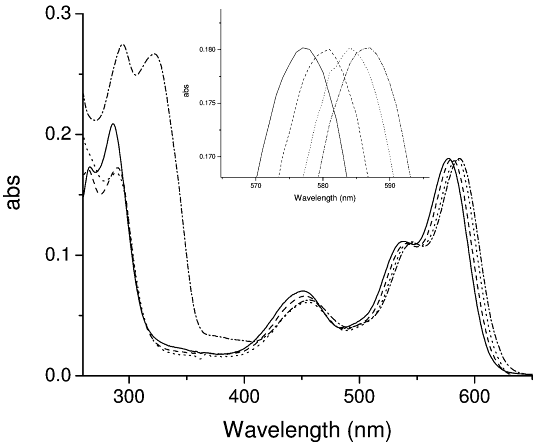

Fig. 5 Absorption spectra of **9** (—), **12a** (---), **12b** (···) and **12c** (-·-) in CH_2Cl_2 at RT. Inset = expansion of the 560 to 600 nm region.

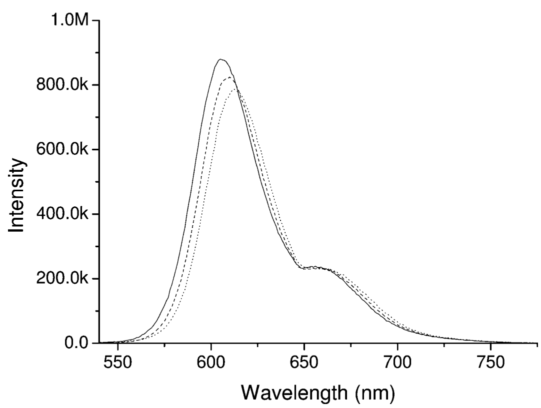

Fig. 6 Emission spectra of **9** (—), **12a** (---) and **12b** (···) in CH_2Cl_2 at RT ($\lambda_{ex} = 450$ nm), showing the decrease in the relative quantum yield of emission.

compound was chosen as a model for the core acceptor unit in photophysical studies.

As for the acceptor unit, a suitable model for the donor part must be identified in order to examine the energy-transfer processes within **12c**. Due to overlap of absorption in **12c** of the coumarin and perylene bisimide components confirmation of the suitability of **4** as a model compound was obtained from comparison of the spectrum of a 2 : 1 molar mixture of **4** and **12b** with the absorption spectrum of **12c** (Fig. 7). The absorption spectrum of the model mixture of **12b** and **4** is almost identical to that of **12c**, with no significant shifts in either the red or the blue region, indicating little or no communication between coumarin and perylene bisimide is present. The location of the maximum at $\lambda = 324$ nm and the intensity of the coumarin **4** absorption coincide with the absorption of the coumarin component of **12c**. Similarly the emission λ_{max} of the model coumarin and the residual emission in **12c** compare well (*vide infra*).

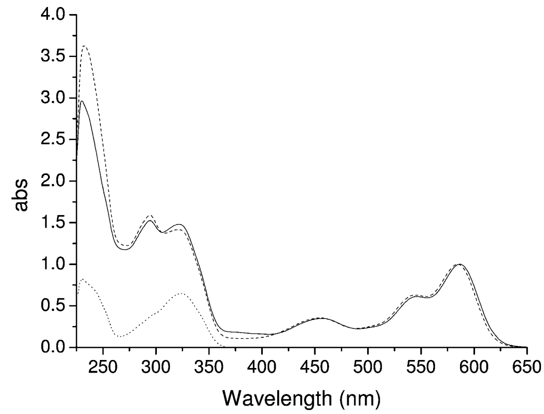

Fig. 7 Absorption spectra of **12c** (—), the 1 : 2 mixture of **12b** and **4** (---), and the spectrum of **4** (···), spectra were recorded in CH_2Cl_2 at RT, the spectra of **12c** and the mixture of **4** and **12b** are normalised to the perylene bisimide absorption maximum ~590 nm.

The fluorescence lifetimes of the model perylene bisimide compounds **9**, **12a** and **12b** ($\lambda_{ex} = 420$ nm), substituted with butyl, phenyl and bridge model **11**, respectively (Fig. 4), show a modest but significant decrease in excited-state lifetimes and are accompanied by a concomitant decrease in the fluorescence quantum yield (Table 1). The trend observed is comparable to the bathochromic shift observed in both absorption and emission spectra. The decrease in emission lifetime is not unexpected and can be rationalised on the basis of the energy-gap law,[21] which predicts a decrease in the nonradiative emission lifetime with a decrease in ground–excited-state energy gap, however it should be noted that the overall difference in the ground and emissive-excited states in this series is 250–300 cm^{-1} in total.[22]

Table 2 Redox potentials of **9** and **12a–c**

Compound	Oxidation/V[a]	Reduction/V[a]		ΔV/V[b]
9	1.25	−0.77	−0.92	2.02
12a	1.28	−0.72	−0.88	2.00
12b	1.31	−0.66	−0.83	1.97
12c	1.33	−0.64	−0.81	1.97

[a] Differential pulse voltammetry. [b] ΔV is the separation between $E_{1/2}$ of the first oxidation and the first reduction (V *vs.* SCE, in CH_2Cl_2–0.1 M $TBAPF_6$).

Redox properties

The redox potentials of perylene bisimides (**9**, **12a–c**, Table 2) were measured by differential pulse and cyclic voltammetry in CH_2Cl_2–0.1 M $TBAPF_6$ between +1.6 V and −1.2 V *vs.* SCE. At anodic potentials a reversible one-electron redox peak ($E_{1/2}$ +1.25 V to +1.33 V *vs.* SCE) is observed for all perylene bisimide-based compounds (Fig. 8). Similarly at cathodic potentials two reversible one-electron redox waves are observed, with the separation between the first process ($E_{1/2}$ −0.64 V to −0.77 V *vs.* SCE) and the second process ($E_{1/2}$ −0.81 V to −0.92 V *vs.* SCE) showing only minimal dependence (~5 mV) on the substituent employed at the imide position. Comparison of **12c** with the model perylene bisimide systems confirms that both the first oxidation and the first and second reduction processes are based on the perylene bisimide core.[6b,20b] Within the potential window examined (+1.6 to −1.6 V *vs* SCE) no redox activity was observed for the coumarin or amide components.

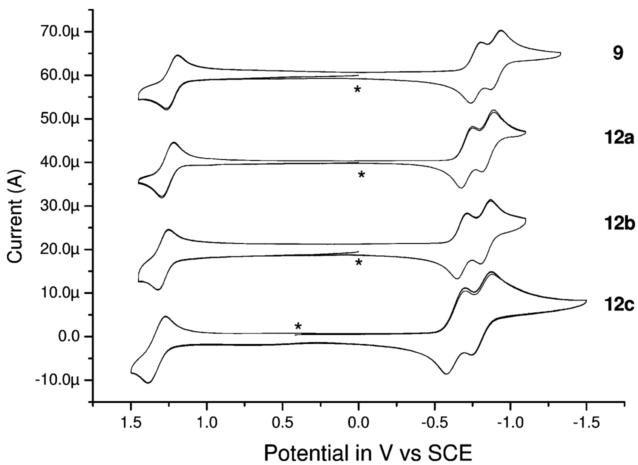

Fig. 8 Cyclic voltammetry of **9** and **12a–c** in CH_2Cl_2/0.1 M $TBAPF_6$ *vs* SCE. The current is offset for clarity.* indicates the open circuit potential.

The correlation between the HOMO–LUMO energy gap determined electrochemically and spectroscopically is well established,[23] providing both the oxidation and reduction involve the same chromophoric unit. The separation (ΔV) between first oxidation and first reduction decreases with decreasing electron-donating ability of the substituent. This indicates a decrease in the HOMO–LUMO energy gap. For **12b** and **12c**, the similarity in the separation (ΔV) indicates a comparable influence on the perylene bisimide core by both imide substituents. Comparison of **9** and **12b** indicates that electron-withdrawing groups destabilise the LUMO to a slightly greater extent than the HOMO, and thereby show a decrease of the HOMO–LUMO gap overall.

Solvent-dependence of spectroscopic properties

Absorption and emission spectra of all compounds were obtained in acetone, dichloromethane and chloroform. For the coumarin model **4** both absorption and emission spectra were identical in dichloromethane and chloroform (aggregation was observed in acetone).

For the perylene bisimide-containing compounds, however, considerable solvent-dependence in both the emission and absorption spectra was observed (Fig. 9 and Table 4). The spectra show a red-shift in both absorption and emission between acetone, dichloromethane and chloroform. The origin of this solvent-dependence can be assigned to the interaction of the imide carbonyls of the perylene bisimide unit with the solvent, and is similar to the effect observed upon substitution at the imide nitrogen (*vide supra*). This solvent effect highlights the influence of the imide carbonyls on the HOMO–LUMO levels of the perylene bisimide core. The nature of the interaction, *vis à vis* HOMO *vs.* LUMO stabilisation, can be estimated from the redox potentials of the compounds in these solvents.

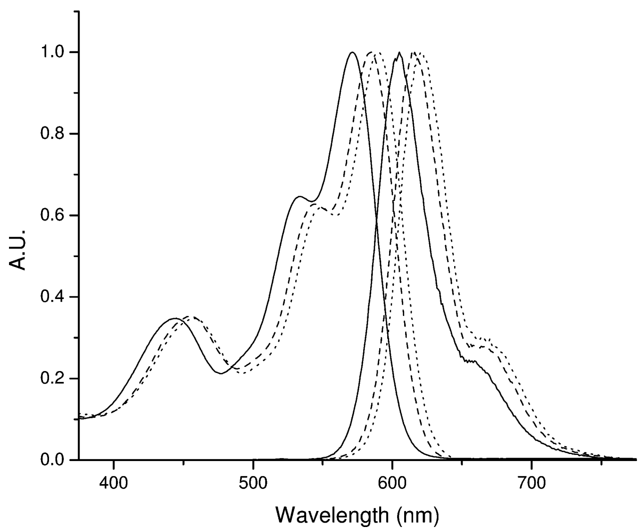

Fig. 9 Absorption and emission spectra of **12b** in acetone (–), CH_2Cl_2 (---) and chloroform (···) at RT (λ_{ex} = 450 nm, spectra normalised for clarity).

The redox properties of the perylene bisimide compounds in dichloromethane and chloroform are shown in Table 3. It is

Table 3 Redox potentials[a] of **9** and **12a–b** in dichloromethane and chloroform

	Dichloromethane		Chloroform	
	$E_{1/2}$	ΔV/V	$E_{1/2}$	ΔV/V
9	1.25, −0.77, −0.92	2.02	1.28, −0.87, −1.03	2.15
12a	1.28, −0.72, −0.88	2.00	1.32, −0.80, −0.99	2.12
12b	1.31, −0.66, −0.83	1.97	1.32, −0.72, −0.91	2.04
12c	1.33, −0.64, −0.81	1.97		

[a] Determined by differential pulse voltammetry (V *vs.* SCE, in respective solvent–0.1 M $TBAPF_6$)

Table 4 Solvent-dependence of the absorption and emission maxima of the perylene bisimide emission ($\lambda \sim 580$ nm) of **9** and **12a–c**

	Absorption[a] (λ_{max})/nm			Emission[a,b] (λ_{max})/nm		
	Acetone	CH_2Cl_2	$CHCl_3$	Acetone	CH_2Cl_2	$CHCl_3$
9	568	577	585	603	608	620
12a	568	580	588	603	614	622
12b	571	584	590	603	616	623
12c	573	587	593	606	618	626

[a] Measurements taken at RT [b] $\lambda_{ex} = 450$ nm.

apparent from the shift in first-reduction potential (*vs.* SCE) going from dichloromethane to chloroform for each separate compound (**9**, **12a–c**) that the LUMO level is affected by the solvent to only a slightly larger extent than the HOMO level. A key aspect of energy transfer is the relative importance of through-bond and through-space contributions to the overall interaction between the donor and acceptor units. Typically the through-bond contribution is estimated by comparison of the spectroscopic properties of the separate donor and acceptor component with those of **12c**. It is clear that although minor differences in the absorption and emission spectra between the 2 : 1 mixture (of **4** and **12b**) and **12c** are observed, these differences are comparable to the effect of local solvent environment.

The molecular geometry and the orbital-energy diagrams of **9**, **12a** and **12b** were calculated using the hybrid Hartree–Fock density functional method (B3LYP/6-31G(d)).[24] The *tert*-butyl groups on the phenol bay substituent were replaced by methyl groups, for **9** instead of a butyl group a methyl was used and for **12b** the piperidine groups were replaced by dimethylamine substituents, this was done to increase symmetry and to reduce calculation cost, all replacement substituents were selected to have minimal impact on the electronic structure. Molecular orbital diagrams of **9**, **12a** and **12b** show a considerable contribution of the imide carbonyls to both the HOMO and LUMO of the model compounds (ESI†). It is clear that the imide substituents are not involved in the frontier orbitals of the perylene compounds examined despite holding a strong influence over the electronic character of the carbonyl bonds. This suggests that the effect of both the solvent and the imide substituents on the electronic properties is due to the perturbation of electron density on the carbonyl groups.

Energy transfer

The absorption spectrum of the coumarin substituted branch **4** in CH_2Cl_2 at RT shows an absorption maximum at λ = 324 nm (Fig. 7). At this wavelength the absorption of the perylene bisimide model is low (Fig. 5), allowing for direct excitation of the donor unit with minimal direct excitation of the perylene bisimide. In order for energy transfer to occur *via* a Förster energy-transfer mechanism, overlap of the donor-emission spectrum and acceptor-absorption spectrum is required. The emission of **4** in CH_2Cl_2 at RT shows a maximum at 394 nm and overlaps with the absorption of the perylene bisimide acceptor unit (Fig. 10).

The emission spectra of a 2 : 1 mixture of **4** and **12b**, and of **12c** were measured in CH_2Cl_2 at RT (Fig. 11). Excitation at λ_{ex} = 450 nm results in perylene bisimide emission of similar intensity at λ_{em} = 616 nm for both systems (not shown). This confirms that the spectroscopic properties of the perylene bisimide core are unaffected by the covalent attachment of the coumarin. Similarly, upon excitation at λ_{ex} = 322 nm, corresponding to the λ_{max} of the coumarin absorption, both the mixture and **12c** show emission at λ_{max} = 394 nm (coumarin emission) and 616 nm (perylene bisimide emission). The intensity of the coumarin emission in both systems is very different, however. The reduced intensity of the coumarin emission, observed for **12c**, indicates quenching of the coumarin emission is taking place (the coumarin Φ_{fl} decreases from 0.5 to <0.03, Table 1). By contrast, the intensity of the perylene bisimide emission of **12c** is increased compared to that in the model system. Hence intramolecular energy transfer from the coumarin to the perylene bisimide core is taking place in **12c**.

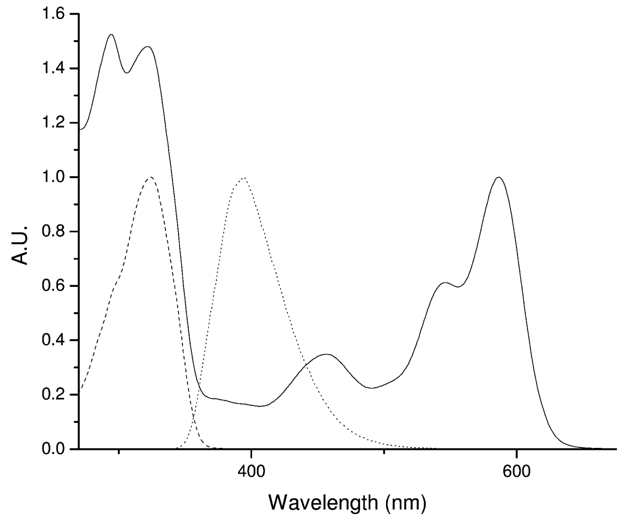

Fig. 10 Absorption and fluorescence spectra of **12c** (abs —) and **4** (abs ---, fl ···, λ_{ex} = 322 nm) normalised to **12c** absorption maximum at λ = 587 nm in CH_2Cl_2 at RT.

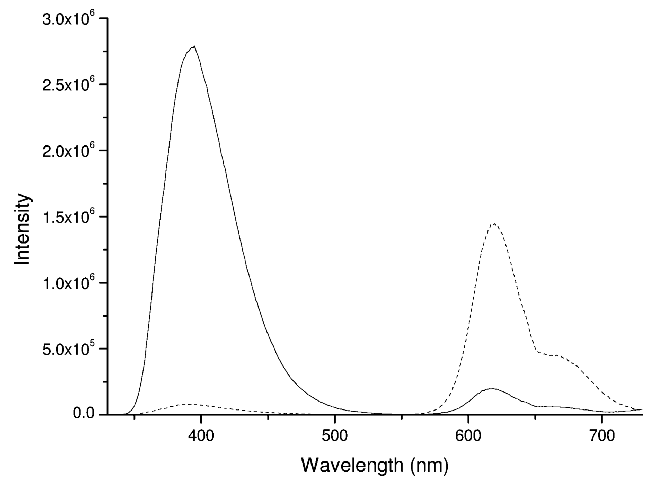

Fig. 11 Emission spectra corrected for the absorption at λ_{ex} = 322 nm of the model mixture (2 : 1 mixture of **4** (3×10^{-5} M) and **12b** (1.5×10^{-5} M), λ_{ex} = 322 nm, —), and **12c** (0.5×10^{-5} M, λ_{ex} = 322 nm, ---) in CH_2Cl_2 at RT.

The absence of intermolecular energy transfer was confirmed through excitation spectroscopy (Fig. 12). The excitation spectrum of **12c** matches the corresponding absorption spectrum closely

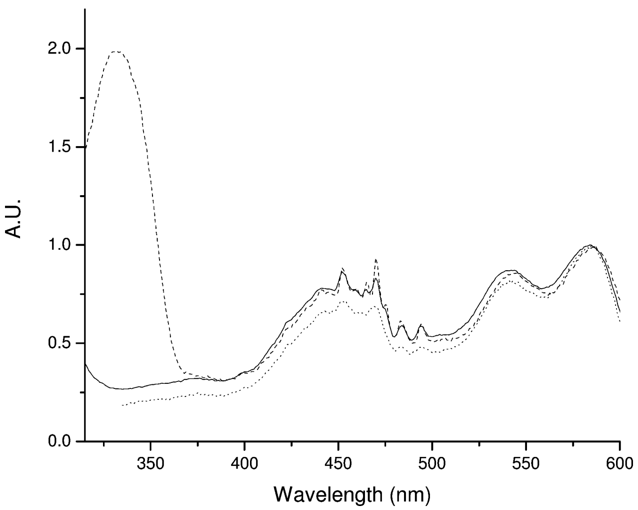

Fig. 12 Excitation spectra of **12b** (—), **12c** (---), and a 2 : 1 mixture of, respectively, **4** and **12b** (···) in CH_2Cl_2 at RT, normalised at the perylene bisimide absorption maximum at 586 nm.

and, importantly, shows the contribution of the coumarin absorption to the perylene bisimide emission in **12c**. Comparison of the excitation spectra of **12b** and the 2 : 1 mixture of **4** and **12b** shows that the free coumarin does not contribute to emission of the perylene bisimide model compound. Hence, it is unlikely that intermolecular energy transfer occurs in solution for **12c**.

Preliminary time-resolved emission spectroscopy confirms that energy transfer from the coumarin donor units to the perylene bisimide acceptor core is fast (<15 ps, Fig. 13). The presence of four donor coumarin units and the non-zero absorption of the perylene bisimide unit itself in the near UV region opens the possibility that several components of the system can be pumped optically to an electronically excited state within the lifetime of the perylene bisimide acceptor excited state, resulting in potentially complex excited-state behaviour. Under the low excitation intensity conditions employed here, however, statistically only one unit in the array is excited at any one time (*i.e.*, either one of the four coumarin donor units or the perylene acceptor core itself). Hence the rapid decay of the coumarin emission and the concomitant rise time of the perylene bisimide component observed by time-resolved spectroscopy provides a strong indication that energy transfer from the coumarin to the perylene bisimide is efficient.

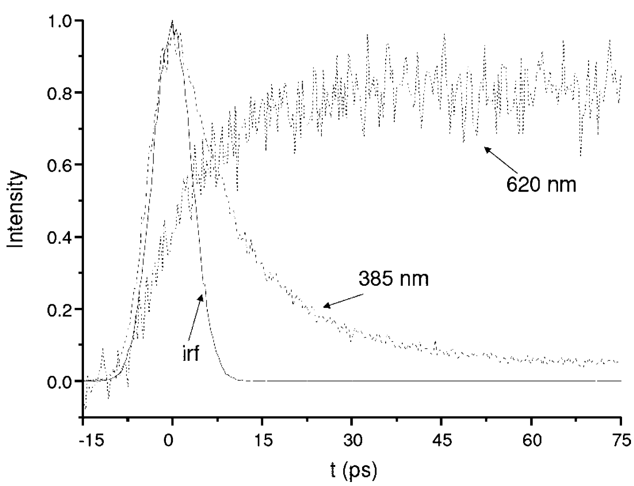

Fig. 13 Time-resolved emission spectroscopy of **12c** in $CHCl_3$. irf-instrument response function, λ_{em} 385 nm (coumarin unit), λ_{em} 620 nm (perylene bisimide unit). Excitation wavelength $\lambda_{ex} = 325$ nm.

Conclusions

In understanding and characterising energy-transfer processes it is essential that the models used for comparison with the dendritic system are suitable. The imide substituent is expected to have a negligible effect on the properties of the perylene bisimide core; however, it is clear from comparison of **9** with **12b** that a significant shift in the absorption spectrum results from a change in the imide substituents. Differences between the absorption spectra of **12c** and model compounds **9**, **12a** and **12b** become less for the imide-substituted models, which are structurally most similar to branch unit **4** used in **12c**. This is quite evident when considering the trends observed in the absorption spectra, but can also be seen when comparing the redox properties. Hence **12b** is the most suitable model compound for the acceptor unit of the donor–acceptor system **12c**. The remaining differences (~2 nm shift) can be rationalised by considering the small differences in local environment, most likely caused by the branches, and are much smaller than differences observed with different solvents (*i.e.* upon changing from dichloromethane to chloroform, a ~10 nm shift is observed).

These small differences suggest that through-bond orbital interaction is minimal if indeed it is present and hence through-bond energy transfer is unlikely. The model mixture of **4** and **12b** also shows that the energy transfer is not due to trivial (intermolecular) energy transfer, since irradiation at the λ_{max} of **4** shows no increase of the perylene bisimide emission compared to a solution of **12b** irradiated at the same wavelength. Irradiation of **12c** at the λ_{max} of **4** shows a clear increase in fluorescence of the perylene bisimide, indicating transfer of energy from the coumarin donor to the perylene bisimide acceptor. This is confirmed by comparison of the excitation spectra of **12c** and model mixture of **4** and **12b**, which show that the energy originates from the coumarin donor and not only from the residual perylene bisimide absorption at that excitation wavelength (Fig. 12, the coumarin λ_{max}).

In the present report we have described the synthesis and characterisation of a tetra coumarin donor–perylene bisimide acceptor array. The energy transfer from the donor units to the acceptor was found to be very efficient (>99%) and to take place *via* a through-space mechanism. In addition to the high efficiency of energy transfer, which is comparable to several related systems reported previously,[13,14,15] the donor$_4$–acceptor array shows high stability, and its redox properties indicate that no undesired, and possibly deleterious, photoinduced electron transfer between the donor and acceptor takes place. Importantly, recognition of the sensitivity of the acceptor to both solvent properties and the nature of the imide substituents is critical for excluding a through-bond contribution to the energy-transfer mechanism. An investigation[25] of the picosecond energy-transfer dynamics and the behaviour of the donor–acceptor system under multiphoton excitation conditions is currently in progress.

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