Tuning energy transfer in switchable donor–acceptor systems†

Johannes H. Hurenkamp, Jaap J. D. de Jong, Wesley R. Browne, Jan H. van Esch*‡ and Ben L. Feringa*

Received 11th December 2007, Accepted 23rd January 2008
First published as an Advance Article on the web 21st February 2008
DOI: 10.1039/b719095f

The synthesis and characterisation of a coumarin–dithienylcyclopentene–coumarin symmetric triad (CSC) and a perylene bisimide–dithienylcyclopentene–coumarin asymmetric triad (PSC) are reported. In both triads the switching function of the photochromic dithienylcyclopentene unit is retained. For CSC an overall 50% quenching of the coumarin fluorescence is observed upon ring-closure of the dithienylcyclopentene component, which, taken together with the low PSS (<70%), indicates that energy transfer quenching of the coumarin component by the dithienylcyclopentene in the closed state is efficient. Upon ring opening of the dithienylcyclopentene unit the coumarin emission is restored fully. The PSC triad shows efficient energy transfer from the coumarin to the perylene bisimide unit when the dithienylcyclopentene unit is in the open state. When the dithienylcyclopentene is in the closed (PSS) state a 60% decrease in sensitized perylene bisimide emission intensity is observed due to competitive quenching of the coumarin excited state and partial quenching of the perylene excited state by the closed dithienylcyclopentene unit. This modulation of energy transfer is reversible over several cycles for both the symmetric and asymmetric tri-component systems.

Introduction

Energy (ET) and electron (E_nT) transfer between molecular entities is of continuing interest in the development of molecular based photonic systems, including photovoltaics,[1] molecular electronics[2] and sensor technologies.[3] The excellent efficiency in energy and electron transfer between donor and acceptor components in the photosynthetic apparatuses of plants and bacteria is achieved through the optimal supramolecular spatial arrangement and energetic matching of donor and acceptor units.[4] Achieving such control represents a considerable challenge in synthetic systems, where the tight organization exerted by nature through membrane and protein structures is not present *a priori*.[4,5]

Efficient energy transfer in synthetic donor acceptor systems can be achieved either by through-bond (superexchange) interactions or by through-space energy transfer. Depending on the mechanism of through-space energy transfer (*e.g.*, Dexter[6] or Förster[7] energy transfer) between donor and acceptor chromophoric units, the efficiency is dependent on the absorption cross-section of the energy acceptor and its overlap with the fluorescence spectrum of the donor unit and also on their spatial arrangements. The electronic properties of the donor and acceptor units can be tuned synthetically to achieve an optimal energetic overlap. However, control over the spatial and orientational arrangement between components is often more difficult to achieve. Overall the approaches taken to control this latter aspect can be divided into two groups—*i.e.* the covalent and non-covalent (supramolecular) arrangement of donor–acceptor units. Both approaches have seen considerable success in achieving efficient energy transfer and in furthering our understanding of the physical basis of, *e.g.*, Förster resonance energy transfer (FRET).[8]

Previously, we have shown that efficient energy transfer can be achieved in a coumarin donor–perylene bisimide acceptor based system.[9,10] In this tetra-coumarin–perylene bisimide system, we demonstrated that energy transfer with an efficiency of >95% could be achieved with good stability even under conditions of high near-UV irradiation flux, without requiring a through-bond interaction between the donor and acceptor components. Furthermore, careful matching of the energetics of the donor and acceptor units avoided potentially deleterious competing electron transfer processes. However, energy transfer in this molecule, although efficient, is not subject to post-synthetic control, *i.e.* the energy transfer efficiency from the donor coumarin units to the perylene bisimide acceptor cannot be altered or modulated reversibly after synthesis.

Controlling energy transfer post-synthetically, *e.g.*, by changing the direction and efficiency of the process, represents an interesting, albeit considerable, challenge. The incorporation of an addressable component into supramolecular systems capable of attenuating energy transfer from an energy donor to an energy acceptor would allow for modulation of the emission output of the donor–acceptor system. Control over fluorescence intensity has been demonstrated by several groups, and, typically, this is achieved through quenching of the fluorescence of the chromophore by an additional unit,[11] whose electronic structure can be changed upon external perturbation, *e.g.*, by photo-[12,13] or electrochemical[14] switching, pH change,[3,15] or by disconnection of a quenching unit.[16]

Dithienylcyclopentene switches, which belong to a class of photochromic switches that show potential as photoswitchable fluorescence quenching units, are suitable candidates to impart functionality in these donor–acceptor systems. These photochromic

Stratingh Institute for Chemistry and Zernike Institute for Advanced Materials, Faculty of Mathematics and Natural Sciences, University of Groningen, Nijenborgh 4, 9747AG Groningen, The Netherlands. E-mail: j.h.vanesch@tudelft.nl, b.l.feringa@rug.nl; Fax: 0031-50-3634296; Tel: 0031-50-3634235

† Electronic supplementary information (ESI) available: UV–Vis and emission spectra following irradiation. See DOI: 10.1039/b719095f

‡ *Present address:* Delft ChemTech, Technical University Delft, Julianalaan 136, 2628 BL, Delft, The Netherlands

switches undergo a photochemical cyclization reaction upon irradiation with UV light, which is reversible upon irradiation with visible light (Fig. 1). Dithienylcyclopentenes show sufficient stability, good to very good photostationary states (PSS) and the two states have very different absorption spectra, which are both thermally stable.[17] The synthetic routes, which are available,[18] facilitate attachment of substituents (in this case chromophores).

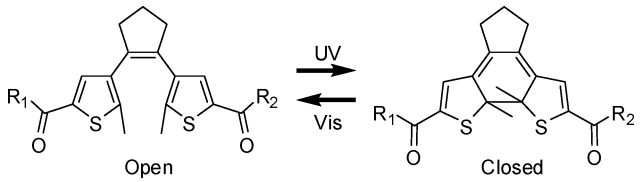


Fig. 1 Schematic representation of the ring-open and ring-closed state of a dithienylcyclopentene switch.

Indeed, dithienylcyclopentenes have been employed successfully already as fluorescence quenchers, examples of which have been reported by the groups of Lehn,[19] Irie,[20] Tian[21] and Branda.[22] However, control of energy transfer efficiency between an energy donor and acceptor pair by a third, addressable, component allows for more versatile control of excited state properties, such as the triad system reported by Walz *et al.*[23] This approach to switchable triad systems has been demonstrated in systems involving electron transfer also,[24] however, the present work focuses on through-space energy transfer. In this contribution we report a covalently linked donor–switch–acceptor triad based on a coumarin (donor), a dithienylethene (switch) and a perylene bisimide (acceptor) unit. The energy transfer between the donor and acceptor units can be redirected by photochemical isomerization of the central 'switching' unit. In the open form, the dithienylcyclopentene acts as a photophysically innocent bridging unit. In the closed form it acts to quench the emission of the coumarin donor and, to a lesser extent, the perylene bisimide acceptor, thereby modulating the luminescence output of the perylene bisimide unit (Fig. 2), by reducing the efficiency of energy transfer from the coumarin donor to the perylene acceptor.

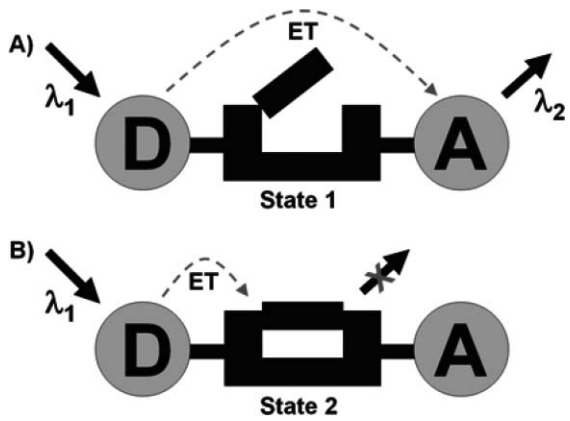
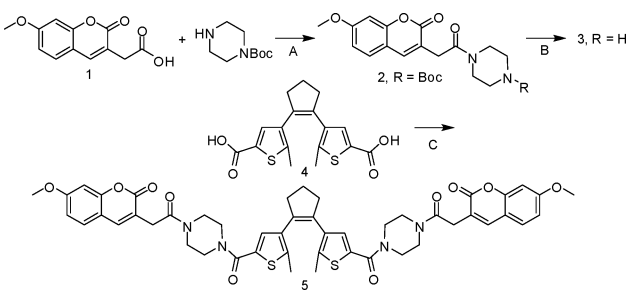


Fig. 2 Schematic representation of a donor–switch–acceptor triad in two different states: (a) the switch is in the open State 1: excitation of the donor (D), energy transfer to the acceptor (A), followed by sensitized emission. (b) The switch is in the closed State 2: when D is excited the energy is quenched by the switch and sensitized emission is prevented.

Results

Synthesis

The symmetric triad, consisting of two coumarin donors and a central dithienylcyclopentene unit, was prepared to demonstrate the quenching concept for the selected donor and switchable-acceptor chromophores (Scheme 1). It was decided to use amides in combination with piperazines as a 'molecular resistor' (*i.e.* similar to the use of adamantanes[20a] or ethers[25] in other multicomponent systems) to construct a symmetric triad, in which the coumarin chromophore is electronically decoupled from the dithienylcyclopentene. This approach was used successfully already in building a tetra-coumarin–perylene bisimide system.[10] The amide coupling method used here to construct the substituted dithienylcyclopentene photochromic switching units has been employed successfully in the synthesis of switchable gelator systems also.[26]

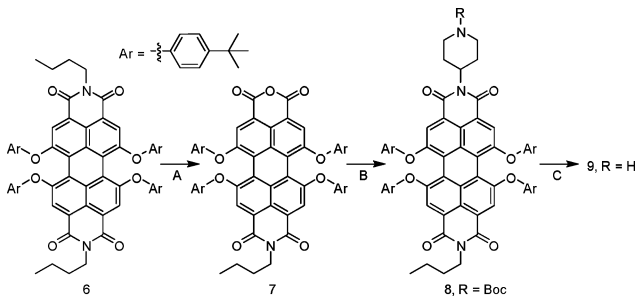


Scheme 1 Synthesis of CSC **5**: (A) CDI, CH_2Cl_2, RT (92%); (B) CF_3COOH, CH_2Cl_2 (quant.); (C) 1. CDMT, NMM, CH_2Cl_2, 0 °C, 2. NMM, **3**, (16%).

7-Methoxycoumarin-3-acetic acid **1** was coupled to mono Boc protected piperazine using the amide coupling reagent 1,1′-carbonyldiimidazole (CDI),[27] which allows for straightforward workup and subsequent purification by column chromatography. The coumarin *N*-Boc-piperazine **2** was deprotected subsequently with trifluoroacetic acid (TFA). Two equivalents of the free amine coumarin piperazine **3** were coupled to the dicarboxylic acid switch **4** using 2-chloro-4,6-dimethoxy-1,3,5-triazine (CDMT), a reagent, which has been found to give good yields in combination with the dicarboxylic acid switch,[26] and *N*-methyl-morpholine (NMM) in CH_2Cl_2 to yield the pure coumarin–switch–coumarin triad (CSC) **5** in 16% yield (non-optimized) after purification by column chromatography (Scheme 1).

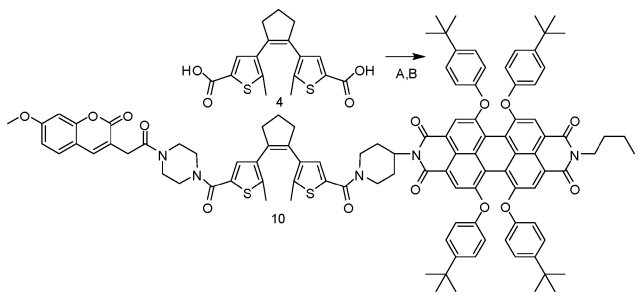
A switch-acceptor unit was constructed, using an amine substituted perylene bisimide **9** (Scheme 2), which can be coupled to the dithienylcyclopentene diacid **4**. Perylene bisbutylimide **6**[28] was saponified partially to provide a mixture of the perylene-bis-anhydride and the perylene-mono-imide-monoanhydride (~2 : 1, respectively, as determined by ^{1}H NMR spectroscopy).[29] The mixture was condensed with 4-amino-1-Boc-piperidine,[30] to yield a mixture of substituted perylene bisimides with either two piperidines *or* one butyl and one piperidine group at the imide positions. The mixture was separated chromatographically providing the mono *N*-Boc-piperidine mono butyl perylene bisimide **8** in 8.6% yield from the perylene bis-butylimide **6** (Scheme 2).

Attempts to mono substitute the diacid dithienylcyclopentene **4**, with the coumarin piperazine **3** followed by coupling to



Scheme 2 Synthesis of mono piperidine perylene bisimide **9**: (A) KOH, H_2O, i-PrOH, 15 h (yield n.d.); (B) 4-amino-1-Boc-piperidine, toluene, 120 °C, 24 h (8.6% from **6**); (C) CF_3COOH, CH_2Cl_2 (quant.).

the perylene bisimide **9** were unsuccessful due to difficulties in purification of the mono acid following the first coupling step. Therefore, it was decided to use a one step procedure with equimolar amounts of the chromophores followed by isolation of the desired compound by column chromatography. First one equivalent of the perylene-mono-piperidine-mono-butyl **8** was deprotected using TFA and the product **9** (1 equivalent) was coupled, together with the coumarin piperazine **3** (1 equivalent) to the diacid dithienylcyclopentene photochromic switch **4** (1 equivalent) to give, in addition to the homo-coupling products, the target perylene–switch–coumarin triad (PSC) **10** in 4.4% yield (non-optimized, Scheme 3).



Scheme 3 Synthesis of PSC **10**: (A) CDMT, NMM, CH_2Cl_2, 0 °C; (B) NMM, 1 eq **3**, 1 eq **9**, 24 h.

The model compound piperidine–dithienylcyclopentene–piperidine (pipSpip **11**, Fig. 4, right) was prepared by similar methods as for CSC **5**. All compounds were purified by column chromatography and characterized with ^1H and ^{13}C NMR spectroscopy and (MALDI-TOF) mass spectrometry (see experimental section for details).

Electronic and photochemical properties

Coumarin–switch–coumarin triad (CSC) 5. The absorption spectrum of CSC **5** in the open and closed (*i.e.* at the photostationary state (PSS) obtained by irradiation at $\lambda_{exc} = 312$ nm, $PSS_{312\,nm}$) form are shown in Fig. 3. The spectra show features of both coumarin and open or closed switch and the maxima correspond closely to those of the model compounds indicating that no direct, or through-bond, electronic communication between the switch and the coumarin is present (Fig. 3 and Table 1). Although at 298 K, irradiation at $\lambda_{exc} = 312$ nm resulted in 10–20% decomposition per cycle, at 220 K, photochromic switching was fully reversible.

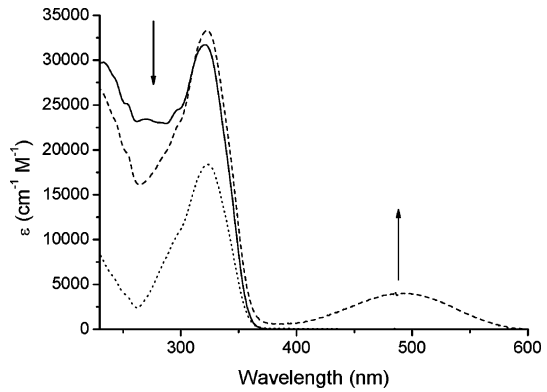


Fig. 3 Absorption spectra of CSC **5** open (—), CSC $PSS_{312\,nm}$ (---) irradiated at 220 K with $\lambda_{312\,nm}$, and coumarin model **2** are shown (···). The spectra were recorded at RT in CH_2Cl_2.

Comparison of the difference spectrum obtained by subtraction of the spectra of **5** in the open form and in the $PSS_{312\,nm}$ with the difference spectrum of the closed form of the model compound **11** shows the similarity between the two systems, confirming that the change in absorption observed upon irradiation at 220 K[31] is due to photochemical ring closure and that the photochromism of the dithienylcyclopentene is retained in the triad (Fig. 4).

CSC **5** can undergo several ring opening–closing cycles with a near complete recovery in the absorption spectrum of the open form after each cycle (see ESI†).[32]

The fluorescence spectrum of the open form of **5** (λ ~390 nm), is identical to that of the free coumarin (Fig. 5). As for absorption spectroscopy, photochemical ring closure results in changes to the luminescence properties of **5**. Irradiation at $\lambda_{312\,nm}$ results in a decrease in the intensity of the characteristic coumarin emission by

Table 1 Absorption and emission spectra of CSC **5** and PSC **10** open and $PSS_{312\,nm}$

	Compound	Absorption[a] λ_{max}/nm (10^3 ε/cm^{-1} M^{-1})	Emission[a] λ_{max}/nm
2	Coumarin pip Boc	322(18.3)	393
6	Perylene bisimide butyl	266(40.6), 286(49.6), 451(16.7), 539(26.7), 577(43.1)	608
11	pipSpip open	239(18.0)	
11	pipSpip $PSS_{312\,nm}$[b]	236(13.6), 487(29.2)	
5	CSC open	321 (31.7)	394
5	CSC $PSS_{312\,nm}$[b]	323 (33.3), 493 (4.0)	395
10	PSC open	267 (50.2), 286 (54.2), 452 (13.4), 540 (22.4), 579 (36.2)	391, 612
10	PSC $PSS_{312\,nm}$[b]	267 (47.5), 286 (52.7), 453 (14.4), 540 (23.2), 579 (36.7)	391, 613

[a] Measurements taken in CH_2Cl_2 at RT. [b] At RT after irradiation with $\lambda_{312\,nm}$ light at 220 K to PSS.

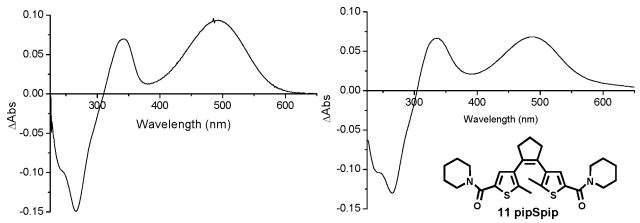


Fig. 4 Left: the UV–Vis difference spectrum obtained by subtraction of the spectrum of the CSC **5** $PSS_{312\,nm}$ state from the spectrum of the CSC **5** open form recorded at 298 K; the PSS was obtained by irradiation with $\lambda_{312\,nm}$ at 220 K. Right: the difference spectrum obtained by subtraction of the spectrum of the pipSpip **11** $PSS_{312\,nm}$ state from the spectrum of the pipSpip **11** open form recorded at 298 K; the PSS was obtained by irradiation with $\lambda_{312\,nm}$ at 220 K.

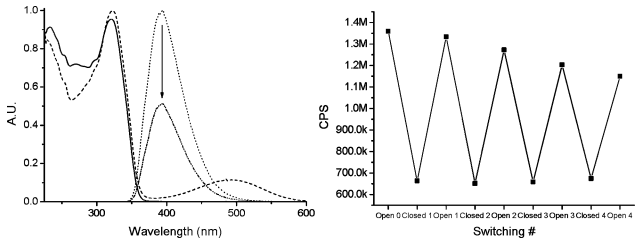


Fig. 5 Left: absorption spectra of **5** open (—) and CSC **5** $PSS_{312\,nm}$ (---), and fluorescence spectra of **5** open ($\cdots$) and **5** $PSS_{312\,nm}$ (---). Right: effect of ring closing and subsequent opening on the fluorescence at $\lambda = 394$ nm (ring closing with $\lambda_{exc} = 312$ nm at 220 K and opening with $\lambda > 400$ nm at 298 K). Spectra recorded in CH_2Cl_2 at 298 K.

50%, which is reversed by irradiation at $\lambda > 400$ nm. This change is not observed when opening and closing a 2 : 1 mixture of the coumarin model **2** and **11**, thus excluding trivial or radiative energy transfer being responsible for the changes seen in the symmetric triad **5**.

The absence of a change in the absorption of the coumarin band in the spectrum of **5** upon ring closure of the dithienylcyclopentene switching unit indicates that the ring closing does not perturb the electronic structure of the coumarin moieties. Hence the decrease in emission intensity can be assigned to energy transfer quenching by the dithienylcyclopentene unit in the closed state. Indeed the absorption spectrum of the closed dithienylethene unit shows good spectral overlap with the emission spectrum of the coumarin; a prerequisite for energy transfer (Fig. 5).

In the open state, the emission of **5** ($\lambda_{exc} = 337$ nm, $\lambda_{em} = 420$ nm) decays monoexponentially with a fluorescence lifetime of 1.1 ns. At the $PSS_{312\,nm}$, in which a mixture of the open and closed form of the switch are present, it is no longer possible to fit the emission decay with a monoexponential function. A biexponential fit provided the expected decay of the coumarin emission 1.1 ns and a second cross-correlated component, *i.e.* a component with a decay lifetime less than the resolution of the instrument (500 ps).[33] This latter component can be attributed to emission from the coumarin in the closed form of **5** in which efficient energy transfer results in the coumarin emission lifetime being limited by the rate of energy transfer from the excited coumarin to the dithienylcyclopentene unit in the closed state.[10]

The degree of quenching of coumarin fluorescence observed (in this case 50% for **5** at the PSS) is dependent on the open–closed ratio at the PSS state. Separation of a mixture of the open and closed form of **5** by HPLC was unsuccessful. However, for the model compound **11**, separation was achieved and a ratio of 30% open–70% closed was determined for $PSS_{312\,nm}$.[34] This value can be taken as the upper limit for CSC **5** (and for PSC **10**, *vide infra*) since the PSS is dependent on both the quantum yield for ring opening *and* closing, and the relative absorption cross-section of the open and closed forms at $\lambda_{312\,nm}$. Since the dithienylcyclopentene switch is electronically decoupled from the coumarin in **5** the quantum yield of ring opening and of ring closing are not likely to be significantly different between **5** and **11**. However, the coumarin components of **5** absorb at $\lambda_{312\,nm}$ and energy transfer from the coumarin to the closed dithienylcyclopentene component will increase the effective absorptivity of the closed dithienylcyclopentene at this wavelength in comparison to **11**. This will serve to change the photostationary state of **5** at $\lambda_{312\,nm}$ in favour of the open state in comparison to **11**.

Perylene–switch–coumarin triad (PSC) 10. The absorption and emission spectra of the PSC triad are shown in Fig. 6 and Fig. 7, respectively. The absorption spectrum of PSC **10** correlates closely with the spectrum of a 1 : 1 : 1 mixture of the perylene bisimide butyl **6**, pipSpip **11** and coumarin-pip-Boc **2**. The near perfect overlap of the λ_{max} of the perylene bisimide and coumarin components indicates that the amide based bridging units do not allow for significant through-bond electronic communication between the three units or perturbation of the electronic structure of the individual components.

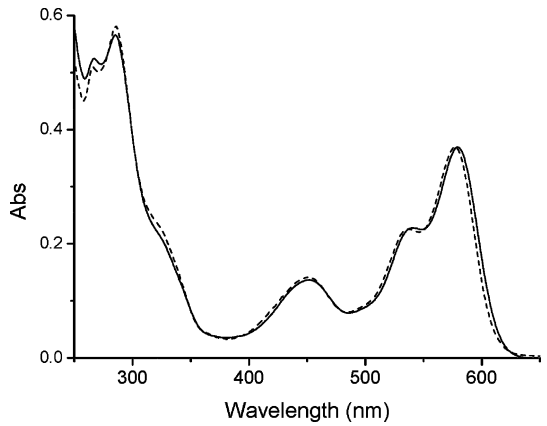


Fig. 6 Absorption spectra of PSC **10** (—) and a 1 : 1 : 1 mixture of the individual components **2**, **6** and **11** (---) recorded in CH_2Cl_2 at 298 K.

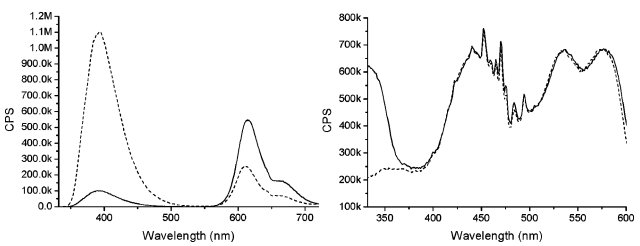


Fig. 7 Left: emission spectra of **10** (—) and of the model mixture 1 : 1 : 1 of **2**, **6** and **11** (---) irradiated at $\lambda_{322\,nm}$ at RT in CH_2Cl_2; spectra were corrected for absorption at the excitation wavelength. Right: excitation spectra of PSC **10** (—) and of the model mixture (a 1 : 1 : 1 ratio of **2**, **6** and **11**) (---) monitored at $\lambda_{620\,nm}$ at RT in CH_2Cl_2.[35]

In contrast to the absorption spectra, the emission spectra of the PSC triad **10** and of a 1 : 1 : 1 mixture of the separate components show considerable differences. When the 1 : 1 : 1 mixture is excited at $\lambda_{322\,nm}$, the emission spectrum shows the characteristic emissions of the coumarin ($\lambda_{em} = 393$ nm) and perylene bisimide ($\lambda_{em} = 609$ nm) components. The excitation spectra recorded at the maxima of the coumarin and perylene bisimide emissions show the characteristic shapes of the coumarin and perylene bisimide absorption spectra, respectively. For the PSC triad **10**, excitation at $\lambda_{322\,nm}$ shows emission characteristic of the coumarin and perylene bisimide components also, however, the coumarin emission is very weak when compared with the 1 : 1 : 1 mixture and the perylene bisimide emission is more intense (Fig. 7, left). That this is due to energy transfer from the coumarin to the perylene bisimide components is apparent from the excitation spectra recorded at the emission maximum of the perylene bisimide component. The excitation spectrum of PSC **10** shows that a large contribution to the emission at $\lambda_{620\,nm}$ originates from an absorption with a maximum at $\lambda \sim 325$ nm, the λ_{max} of the coumarin absorption. This contribution is not seen in the excitation spectrum of the 1 : 1 : 1 mixture. This confirms that in **10** in the open state, efficient intramolecular energy transfer from the coumarin to the perylene bisimide takes place (Fig. 7, right).

Absorption and emission spectroscopy of 10 at the $PSS_{312\,nm}$. The changes in the absorption spectrum on irradiation to the PSS at 312 nm are minor, due to the relatively low molar absorptivity of the switching unit compared with those of the coumarin and perylene bisimide components (Fig. 8). The changes are more apparent in the difference spectra and are very similar to those observed for the model switching unit **11** (Fig. 4 right),[36] and confirms that the dithienylethene unit retains its photochromic behaviour in the PSC triad **10**. As for **5**, ring opening and closing of the switching unit of **10** can be performed over several cycles (see ESI†).

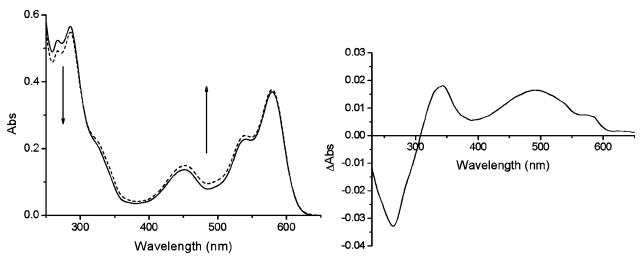


Fig. 8 Left: PSC **10** open (—) and $PSS_{312\,nm}$ (---) irradiated at 220 K[37] with $\lambda_{312\,nm}$ in CH_2Cl_2, spectra recorded at RT. Right: difference spectrum for PSC **10** at $t = 0$ min and PSS after $t = 10$ min irradiation at $\lambda_{312\,nm}$ at 220 K (see Fig. 4 for comparison with **5** and **11**).

The absence of a large overlap of the absorption of the dithienylethene component in the closed state and the emission spectrum of the perylene unit would suggest that energy transfer between the two units would be inefficient. However, comparison of the emission spectra of the perylene unit in the open and $PSS_{312\,nm}$ states (under direct excitation *i.e.* λ_{exc} 450 nm, Fig. 9) shows that the perylene bisimide emission is quenched significantly (21%) upon ring closing. Taking the low photostationary state (*i.e.* <70% closed form) into account, in the closed state the efficiency of quenching of the perylene excited state by the dithienylethene unit is *ca.* 55–65%.

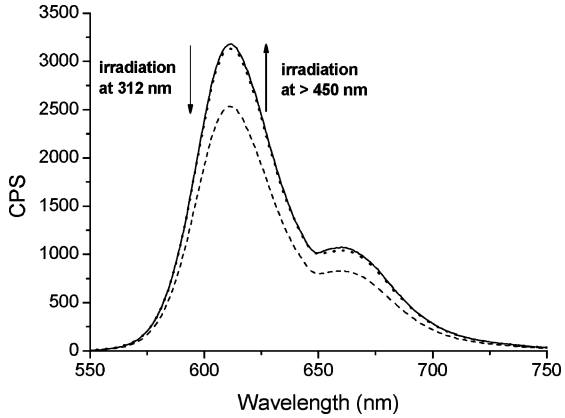


Fig. 9 Emission spectra of PSC **10** in the open state (solid line), after irradiation at $\lambda_{312\,nm}$ to form the $PSS_{312\,nm}$ state (dashed line) and after visible (>450 nm) irradiation to reform the open state (dotted line). All traces were recorded by excitation at $\lambda_{450\,nm}$ in CH_2Cl_2 at RT.

A decrease of 30% in the intensity of the perylene bisimide fluorescence of **10** in its $PSS_{312\,nm}$ is observed (Fig. 10) when excited at the λ_{max} of the absorption of the coumarin ($\lambda = 322$ nm). This could indicate that energy transfer from the coumarin unit is less efficient in the closed state. This decrease, however, is not accompanied by a concomitant increase in the fluorescence of the coumarin component. Hence, the decrease in perylene bisimide emission intensity is due to the introduction of an alternative quenching pathway for the coumarin component, and not a decrease in the overall efficiency of quenching of the coumarin excited state in the triad.

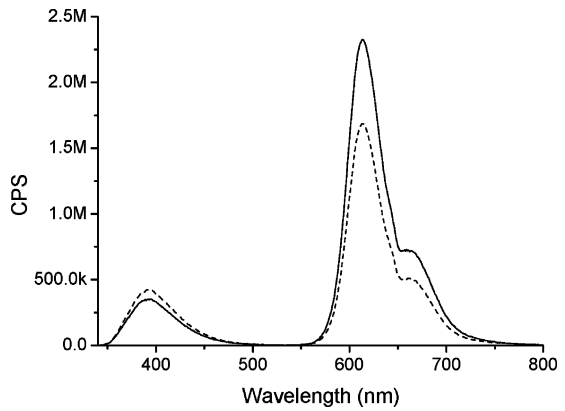


Fig. 10 Emission spectra of PSC **10** open (—) and $PSS_{312\,nm}$ (---) irradiated at 220 K with 312 nm in CH_2Cl_2. All traces were recorded by excitation at 322 nm in CH_2Cl_2 at RT.

The reduction in the intensity of the perylene bisimide component is reversed upon irradiation at λ >400 nm and the closing–opening cycle can be repeated several times with limited degradation (<8% per cycle, Fig. 11). The reversibility of the changes in emission spectrum of **10** confirms that the effect is due to the opening and closing of the dithienylethene switch component of the triad. A steady increase of the coumarin fluorescence ($\lambda_{max} = 391$ nm) is observed with each cycle, which

is assigned to photodegradation of the perylene bisimide unit. Indeed, when irradiating at $\lambda_{254\,nm}$, rapid decomposition of the perylene bisimide with a near complete recovery of the expected emission intensity of the coumarin component is observed (see ESI†).

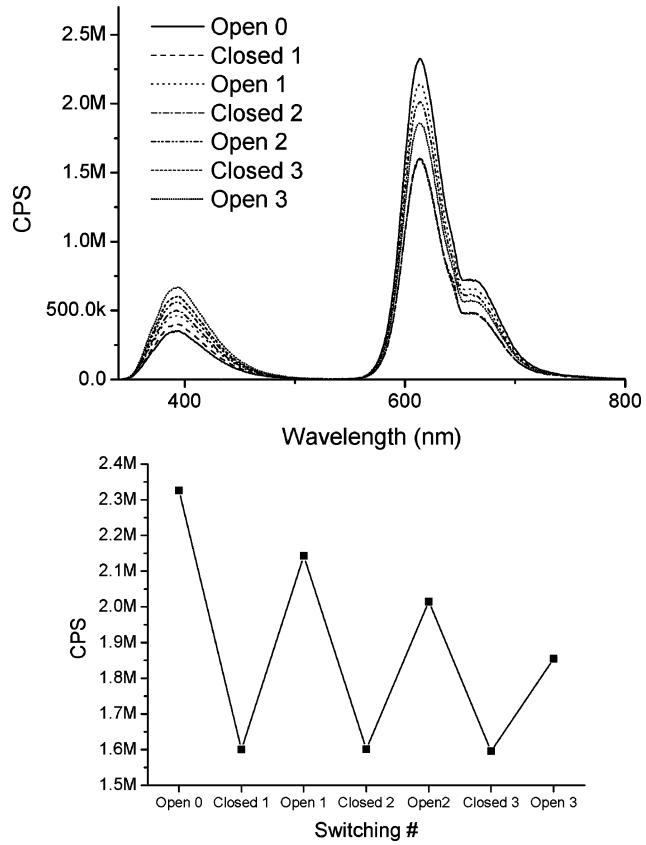


Fig. 11 Above: emission spectra of switching cycles for PSC **10** from PSC open to PSC **10** closed PSS, irradiated with, respectively, $\lambda_{312\,nm}$ at 220 K and $\lambda > 400$ nm light at RT in CH_2Cl_2, compensated for absorption. Below: fluorescence intensity at $\lambda_{614\,nm}$ plotted for three switching cycles of PSC **10** using $\lambda_{312\,nm}$ light at 220 K to close and $\lambda > 400$ nm at RT to open, measurements were performed in CH_2Cl_2 and spectra were recorded at RT.

The fluorescence decay kinetics for the triad show considerable differences, when comparing the open state and $PSS_{312\,nm}$. In the open form, the emission decay of **10** (recorded at $\lambda_{em} = 420$ nm) is biexponential, with a slow component of ~2.0 ns, assigned to the fluorescence decay of free coumarin, and a short (cross-correlated) component, which is attributed to energy transfer (between the coumarin and perylene bisimide unit) rate limited fluorescence decay of the coumarin component of the triad. This decay time is comparable with that observed in the tetra-coumarin–perylene bisimide system reported earlier.[9,10] Compound **10**, at the $PSS_{312\,nm}$, shows biexponential decay kinetics with similar lifetimes and contributions as in the open state.

The emission decay kinetics of **10** in the open state, recorded at λ_{em} 615 nm (*i.e.* the λ_{max} of the emission of the perylene bisimide component), show monoexponential decay kinetics with a decay lifetime of ~7 ns, which corresponds closely to the lifetime of the perylene bisimide model compound **6**. The same value was observed for the PSC **10** $PSS_{312\,nm}$, indicating that the closed form of the switch does not perturb the energy of the emissive excited state of the perylene, *i.e.* the radiative and non-radiative decay rates are unaffected.

Fluorescence decay traces were recorded for **10** in the open, $PSS_{312\,nm}$ and reopened state (Fig. 12). Irradiation of the open state of **10** to the $PSS_{312\,nm}$ (closed) state results in a decrease in emission intensity, however the emission decay lifetimes measured in either state are unaffected.

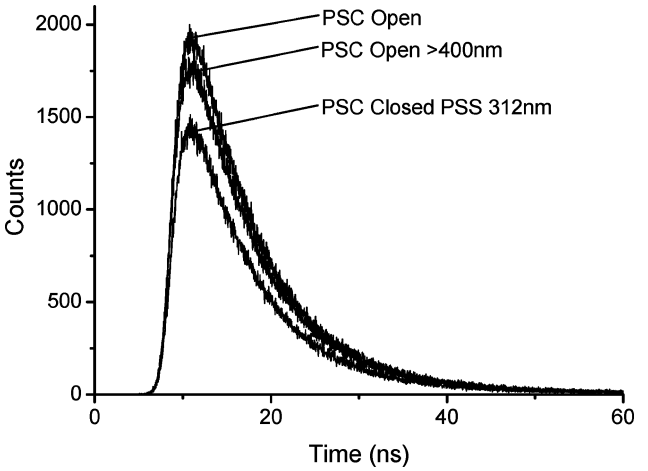


Fig. 12 TCSPC spectra of PSC **10** $PSS_{312\,nm}$ irradiated with $\lambda_{322\,nm}$ light and fluorescence decay counts measured at 615 nm. All traces were recorded over the same acquisition time to enable comparison of the signal intensity, top (black): PSC **10** open, bottom (dark grey): PSC $PSS_{312\,nm}$ by irradiation with $\lambda_{312\,nm}$ light for 4 min, and middle (light grey): PSC **10** open after irradiating the $PSS_{312\,nm}$ form with $\lambda > 400$ nm light for 20 min, all traces recorded in CH_2Cl_2 at RT.

This indicates that even though there is less energy being transferred to the perylene bisimide acceptor from the coumarin donor, this is not caused by a change in the electronic structure of the perylene bisimide. Upon irradiation with $\lambda > 400$ nm to reopen the dithienylcyclopentene switch component, the intensity of the fluorescence increases again, recovering to nearly its original intensity, as observed by emission spectroscopy (Fig. 12).

Discussion

The symmetric CSC triad 5

In the symmetric triad CSC **5**, the ability of the dithienylcyclopentene unit to switch between an open and closed state is apparent from the appearance of the characteristic absorption band of the closed state in the visible region (λ_{max} ~500 nm) upon UV irradiation and its subsequent disappearance upon irradiation with visible light. The decrease in the fluorescence intensity of the coumarin components observed upon ring closing of the dithienylcyclopentene unit can be assigned to energy transfer quenching of the excited coumarin unit by the closed dithienylcyclopentene on the basis of an absence of such an effect in the 2 : 1 mixture of **2** and **11** and the biexponential nature of the emission decay upon ring closure. The incomplete quenching (~50%) of the fluorescence of the coumarin components at the $PSS_{312\,nm}$ is not indicative of inefficient quenching, however, but reflects the low photostationary state achievable for the

dithienylcyclopentene unit, which is less than 70% in favour of the closed form. This is supported by the fluorescence lifetime decay traces where, for the open form, strictly monoexponential behaviour is observed with a lifetime very similar to the free coumarin component, whereas at the $PSS_{312\,nm}$, the fluorescence decay is no longer monoexponential but shows two distinct contributions—a component identical to that observed in the open state and a cross-correlated component with a lifetime considerably less than the instrument resolution (*i.e.* <500 ps) (Fig. 13).

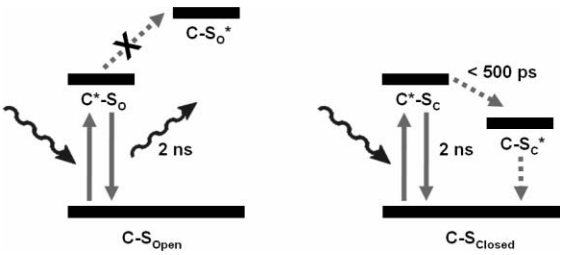


Fig. 13 Energy level diagram of the spectroscopic processes observed in the open and closed state of **5** (C = coumarin, S = dithienylcyclopentene).

The biexponential decay at the $PSS_{312\,nm}$ reflects the presence of both the open form and closed form of the symmetric triad in solution. Nevertheless, it is clear that the dithienylcyclopentene component can act as a switchable efficient 'energy sink' for the coumarin components.

The asymmetric PSC triad 10

The ability to quench the fluorescence of the coumarin by the dithienylcyclopentene component in the closed state but not the open state can be used to modulate the emission output of coumarin–perylene bisimide based donor–acceptor systems.[9,10] In the present report the dithienylcyclopentene unit is incorporated between the energy donating coumarin unit and the energy accepting perylene bisimide unit, *i.e.* in the triad **10**.

The absorption spectrum of PSC **10** is almost identical to that of the 1 : 1 : 1 mixture of **2**, **6** and **11** indicating that the amide units employed to link the three components together do not facilitate ground state electronic communication and that the covalent tethering of the individual components does not result in a perturbation of their electronic properties. Indeed the photochemistry of **11**, with respect to ring opening and closing of the dithienylcyclopentene unit, is retained in **10**. With respect to luminescence, for **10** the covalent attachment of the chromophores does not affect the spectral shape compared with the emission spectra of the separate components. However, the relative intensities of each emission component show substantial changes.

When the emission spectrum of the open form of PSC **10** is compared to that of the model mixture, two aspects are notable. First it is evident that the intensity of the coumarin fluorescence in the model mixture is much higher then in the emission spectrum of **10**. Secondly the intensity of the perylene bisimide acceptor fluorescence is increased significantly in the emission spectrum of **10** compared with **6**. This shows that there is intramolecular energy transfer from the coumarin-donor to the perylene bisimide-acceptor only in the triad system and not in the solution of the mixture of the separate component units.

Comparison of the emission spectra of the open and $PSS_{312\,nm}$ state of PSC **10** shows an intensity decrease of the perylene bisimide emission, which is not accompanied by a proportional increase in emission from the coumarin component. Hence, energy transfer from the coumarin donor is still taking place, but is directed elsewhere. Considering **5**, it is most likely that energy transfer from the coumarin to the closed form of the dithienylcyclopentene unit is taking place. The decrease in emission intensity of **10** upon irradiation to the $PSS_{312\,nm}$ state is ~30% (Fig. 10), however, this does not take into account the direct excitation of the perylene bisimide. Surprisingly, in the closed state however, not only the coumarin emission is quenched but the perylene bisimide excited state is also partly quenched by the dithienylethene. This is unexpected since the overlap of the dithienylethene absorption spectrum and the emission spectrum of the perylene bisimide is negligible.

Overall the modulation of the fluorescence by photochromic switching can be attributed to several possible effects. The ring-closing of the switching unit has two effects, one is an increase in the rigidity of the triad, thereby increasing the average distance between coumarin-donor and perylene bisimide-acceptor. Secondly, by ring closing, a new, low energy chromophore is formed, which allows for competitive (with the perylene bisimide) energy transfer quenching of the coumarin emission, as observed for **5**. That the latter mechanism is most likely to be the major effect is confirmed by the absence of a proportional increase in emission intensity of the coumarin component in the $PSS_{312\,nm}$ state.

In the open state of **10** it is not possible to quench the coumarin excited state *via* the dithienylcyclopentene (open switch) since its lowest excited state lies higher in energy than that of the coumarin (*vide supra*), and the rate of fluorescence decay of the coumarin is limited by the rate of energy transfer to the perylene bisimide unit (Fig. 14).

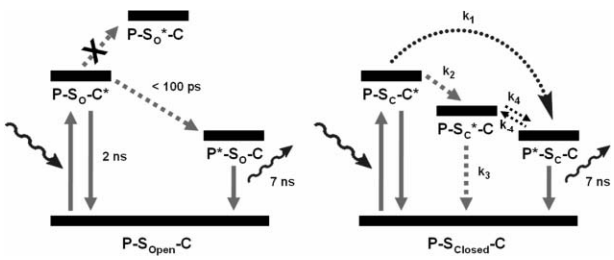


Fig. 14 Energy level diagram of the spectroscopic processes observed in the open and closed state of PSC **10** (P = perylene bisimide, C = coumarin, S = dithienylcyclopentene switch).

In the closed state of **10** there are additional competing energy transfer and decay processes (Fig. 14). From previous results it is known that the energy transfer from the coumarin donor to the perylene bisimide acceptor (k_1) is a fast process (*i.e.* ~11 ps, see ref. 10). For k_2, energy transfer from the coumarin to the closed dithienylcyclopentene, to be competitive, must be of the same order of magnitude or faster, which in this case is probable since a ~60% decrease in fluorescence intensity is observed upon irradiation to the $PSS_{312\,nm}$ of **10**. Once energy has been transferred to the closed dithienylcyclopentene, it can dissipate through a fast non-radiative decay path (k_3) or be transferred to the perylene bisimide (k_4). Energy transfer to the perylene bisimide through

the Förster mechanism is unlikely since the Φ_{fl} for the closed dithienylcyclopentene is low[26] and a high quantum yield is a prerequisite for efficient FRET. Nevertheless it is clear from Fig. 9 that the dithienylethene unit in the closed state can itself quench the emission of the perylene bisimide component (k_{-4}), albeit with low efficiency (55–65%), implying that the proximity of the perylene and closed dithienylethene components is sufficient to allow for energy transfer to take place. This means that energy transferred to the closed dithienylcyclopentene dissipates through a fast non-radiative decay pathway. Thus in the closed state the dithienylcyclopentene component provides a fast and efficient route to quench the coumarin emission as was observed for **5** and as an inefficient route able to quench the perylene emission only partially.

The present system is comparable to the system of Walz *et al.*, who have used energy transfer quenching to influence intramolecular energy transfer in a triad molecule.[23] In that system and in contrast to **10**, the photochromic switch (a fulgimide) is closed and provides the lowest energy state of the system. It is, therefore, able to quench both of the chromophores' excited states (*i.e.* anthracene and coumarin) and acts as an energy sink for all intramolecular processes. For the present system (*i.e.* **10**), the lowest excited state of the photochromic switch in the closed state lies between the donor coumarin and the perylene bisimide acceptor excited states (Fig. 14). Hence it is able to quench the excited state of the coumarin efficiently, however, the perylene bisimide excited state is quenched only partially.

Conclusions

In the present contribution, two energy transfer donor–acceptor systems are reported. In the first system, the function of the dithienylcyclopentene-based photochromic switching unit as a molecular switch, *i.e.* turning coumarin emission on and off, is demonstrated. In the asymmetric PSC triad system **10** we have demonstrated that energy transfer efficiency in a donor–acceptor system can be addressed through modulation of the energy transfer quenching abilities of a photoactive unit. The low PSS achievable (<70%) and the poor photostability at room temperature in the present system, both related to intrinsic properties of the dithienylcyclopentene unit, will be addressed in further studies. Nevertheless, the synthetic approach taken enables connection of the photoactive units covalently without loss of molecular function. These combined observations show that it is possible to build a molecular triad that allows for modulation of the energy transfer in a donor–acceptor system by introducing a switchable selective quencher of the donor unit, thereby allowing control of the emission output.

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,[38] **2**,[9] **3**,[9] **4**[26] and **6**[39] were prepared according to literature. ^{1}H NMR spectra were recorded at 400 MHz; ^{13}C NMR spectra at 101 MHz. All spectra were recorded at ambient temperature, with the residual proton signals of the solvent as an internal reference. Chemical shifts are reported relative to TMS. CI and EI mass spectra were recorded on a JEOL JMS-600 mass spectrometer in the scan range of m/z 50–1000 with an acquisition time between 300 and 900 ms and a potential between 30 and 70 V. MALDI-TOF spectra were recorded on an Applied Biosystems Voyager-DE Pro. UV–Vis absorption spectra (accuracy ±2 nm) were recorded on a Hewlett-Packard UV/Vis 8453 spectrometer. Fluorescence measurements were performed on a SPF-500C (SLM Aminco) or a Jobin-Yvon Fluorolog 3–22 spectrofluorimeter. Luminescence lifetime measurements were obtained using an Edinburgh Analytical Instruments (EAI) time-correlated single-photon counting apparatus (TCSPC) comprised of two model J-yA monochromators (emission and excitation), a single photon photomultiplier detection system model 5300, and a F900 nanosecond flashlamp (N_2 filled at 1.1 atm pressure, 40 kHz) interfaced with a personal computer *via* a Norland MCA card. A 400 nm cut off filter was used in emission to attenuate scatter of the excitation light (337 nm). Data correlation and manipulation was carried out using EAI F900 software version 5.1.3. Emission lifetimes were calculated using a single-exponential fitting function, Levenberg-Marquardt algorithm with iterative deconvolution (Edinburgh instruments F900 software). The reduced χ^2 and residual plots were used to judge the quality of the fits. Lifetimes are ±5%.

(5) Coumarin–switch–coumarin (CSC) triad

Diacid **4** (200 mg, 0.58 mmol) was suspended in CH_2Cl_2 (20 ml) and placed in an ice bath. Subsequently *N*-methylmorpholine (0.13 ml, 1.21 mmol) was added whereupon the solid dissolved. 2-Chloro-4,6-dimethoxytriazine (192 mg, 1.16 mmol) was added and the reaction mixture was stirred for 4 h at 0 °C, after which another two equivalents of *N*-methylmorpholine (0.13 ml, 1.21 mmol) were added followed by **3** (350 mg, 1.16 mmol). Stirring was continued for 1 h at 0 °C, and overnight at room temperature. CH_2Cl_2 (50 ml) was added and the solution was washed with, respectively, 1 M aq. HCl (2 × 20 ml), brine (1 × 20 ml), saturated aqueous bicarbonate solution (1 × 20 ml) and H_2O (1 × 20 ml). The organic phase was dried over Na_2SO_4 and the solvent was removed *in vacuo*. The resulting solid crude product was purified using column chromatography (2% MeOH in CH_2Cl_2, SiO_2), yielding the light yellow solid (85 mg, 0.093 mmol, 16%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.63 (s, 2H), 7.32 (d, J = 8.6 Hz, 2H), 6.82–6.74 (m, 6H), 3.82 (s, 6H), 3.62 (s, 16H), 3.58 (s, 4H), 2.75 (t, J = 7.4 Hz, 4H), 2.10 (s, 6H), 2.09–1.97 (m, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.5 (s), 163.2 (s), 162.3 (s), 161.8 (s), 155.0 (s), 141.8 (d), 139.2 (s), 135.3 (s), 135.2 (s), 132.3 (s), 130.7 (d), 128.5 (d), 119.4 (s), 112.8 (s), 112.5 (d), 100.4 (d), 55.6 (q), 45.8 (t), 41.7 (t), 37.6 (t), 34.1 (t), 23.0 (t), 14.3 (q) ppm. MALDI-TOF MS (MW = 916.28) m/z = 916.46 [M$^+$].

(8) Mono butyl mono *N*-Boc-piperidine perylene bisimide

Partial saponification of *N*,*N*′-dibutyl-1,6,7,12-tetra(4-*tert*-butylphenoxy)perylene-3,4,9,10-tetracarboxylic acid bisimide **6** (3.3 g, 3.0 mmol) was carried out with KOH (75 g, 134 mmol) in a mixture of isopropyl alcohol (500 mL) and H_2O (50 mL) under a dinitrogen atmosphere by stirring at reflux for 13 h, followed by separation of the basic aqueous layer. The organic layer was poured onto an aqueous 10% HCl (1 l) solution and left overnight,

during which the color changed from green to orange to dark red. Filtration and thorough washing and drying, yielded a mixture of perylene bisanhydride and perylene mono butylimide in a ratio of ~2 : 1 (3.3 g) as determined by ^{1}H NMR spectroscopy. This mixture was heated at reflux under a dinitrogen atmosphere in dry toluene (330 ml) with 4-amino-1-Boc-piperidine (2 g, 10 mmol) for 3 d. The solvent was evaporated and the remaining crude product was purified by column chromatography (0.5% MeOH in CH_2Cl_2, SiO_2) providing the mono butyl mono *N*-Boc-piperidine perylene bisimide as a red solid (315 mg, 0.26 mmol, 8.6%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.22 (s, 2H), 8.20 (s, 2H), 7.26–7.20 (m, 8H), 6.87–6.79 (m, 8H), 5.18–5.02 (m, 1H), 4.42–4.05 (m, 3H), 2.91–2.66 (m, 1H), 2.66 (dq, J = 11.8, 3.5 Hz, 2H), 1.72–1.57 (m, 4H), 1.45 (s, 9H), 1.39 (dd, J = 15.1, 7.5 Hz, 2H), 1.29 (s, 36H), 0.94 (t, J = 7.3, 7.3 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.7 (s), 163.4 (s), 155.9 (s), 155.8 (s), 154.4 (s), 152.8 (s), 152.8 (s), 147.2 (s), 132.9 (s), 132.7 (s), 126.6 (d), 122.6 (s), 122.4 (s), 120.5 (s), 120.4 (s), 119.9 (d), 119.8 (d), 119.4 (s), 119.4 (s), 119.3 (d), 119.2 (d), 79.4 (s), 52.0 (d), 44.3 (t), 43.5 (t), 40.3 (t), 34.3 (t), 31.4 (q), 30.1 (t), 28.4 (q), 20.3 (t), 13.7 (q) ppm. MALDI-TOF MS (MW = 1221.6) m/z = 1221.6 [M$^+$].

General deprotection method for BOC protected amines 2 and 8

The Boc protected amine was stirred in a mixture of 1 : 1 CH_2Cl_2–CF_3COOH for 4 h. An equal volume of water was added and the mixture was neutralized by addition of solid $NaHCO_3$, after which the aqueous layer was separated and the organic layer washed with a saturated $NaHCO_3$ solution (aq). The organic layer was dried over Na_2SO_4 and solvent removed *in vacuo*. The product was used in subsequent steps without further purification.

(10) Perylene–switch–coumarin (PSC) triad

Diacid **4** (93 mg, 0.27 mmol) was suspended in CH_2Cl_2 (20 ml) and placed in an ice bath. Subsequently *N*-methylmorpholine (0.06 ml, 0.56 mmol) was added whereupon the solid dissolved. 2-Chloro-4,6-dimethoxytriazine (98 mg, 0.56 mmol) was added and the reaction mixture stirred for 4 h at 0 °C, after which another two equivalents of *N*-methylmorpholine (0.06 ml, 0.56 mmol) were added followed by the deprotected mono butyl mono *N*-Boc-piperidine perylene bisimide **9** (300 mg, 0.27 mmol) and **3** (81 mg, 0.27 mmol). Stirring was continued for 1 h at 0 °C, and overnight at room temperature. CH_2Cl_2 (50 ml) was added and the solution was washed with, respectively, 1 M aq. HCl (2 × 20 ml), brine (1 × 20 ml), saturated aqueous bicarbonate solution (1 × 20 ml) and H_2O (1 × 20 ml). The organic phase was dried on Na_2SO_4 and the solvent was evaporated. The resulting solid crude product was purified using column chromatography (2% MeOH in CH_2Cl_2, SiO_2), providing a dark red solid (20 mg, 0.012 mmol, 4.4%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.20 (s, 2H), 8.19 (s, 2H), 7.61 (s, 1H), 7.29 (d, J = 9.2 Hz, 1H), 7.23 (d, J = 8.9 Hz, 8H), 6.94 (s, 1H), 6.85–6.76 (m, 11H), 5.27–5.17 (m, 1H), 4.48 (s, 2H), 4.13–4.07 (m, 2H), 3.82 (s, 3H), 3.66–3.52 (m, 8H), 2.94 (s, 2H), 2.83–2.62 (m, 6H), 2.15 (s, 2H), 2.02 (s, 2H), 2.09–1.98 (m, 1H), 1.61 (s, 3H), 1.76–1.59 (m, 4H), 1.47–1.32 (m, 2H), 1.29 (s, 18H), 1.82 (s, 18H), 0.93 (t, J = 7.3 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.8, 164.0, 163.6, 163.6, 163.3, 162.5, 162.1, 156.3, 156.1, 155.4, 153.1, 153.0, 147.6, 142.0, 139.6, 138.7, 135.6, 135.6, 135.5, 135.5, 133.5, 133.1, 133.0, 132.6, 131.2, 130.2, 128.7, 126.9, 122.8, 122.71, 120.9, 120.5, 120.3, 120.0, 119.9, 119.7, 119.6, 119.6, 119.5, 113.2, 112.7, 100.7, 55.9, 51.8, 46.1, 42.1, 40.6, 38.2, 37.9, 34.6, 34.4, 31.7, 30.4, 28.7, 23.3, 20.6, 14.7, 14.4, 14.0 ppm. MALDI-TOF MS (MW = 1735.71) m/z = 1735.89 [M+].

(11) PipSpip

11 was synthesized using a procedure similar to CSC **5** using piperidine as amine and starting from **4** (200 mg, 0.58 mmol). Purification provided pipSpip as a cream solid (42 mg, 0.087 mmol, 15%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.84 (s, 2H), 3.59–3.49 (m, 8H), 2.76 (t, J = 7.4 Hz, 4H), 2.05 (s, 6H), 2.09–1.97 (m, 2H), 1.70–1.59 (m, 4H), 1.59–1.47 (m, 8H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.0 (s), 138.1 (s), 135.1 (s), 134.9 (s), 133.4 (s), 129.9 (d), 37.9 (t), 26.0 (t), 24.6 (t), 22.9 (t), 14.3 (q) ppm. MS(EI) for $C_{27}H_{34}N_2O_2S_2$ m/z 482 [M$^+$], HRMS calcd for $C_{27}H_{34}N_2O_2S_2$: 482.2061, found: 482.2073.

Acknowledgements

The research was financially supported by the Zernike Institute for Advanced Materials (JHH, JJDdJ) and Nanoned (WRB). The authors acknowledge T. Tiemersma-Wegman for help with the HPLC analysis. Prof. J. G. Vos and Dr W. Henry (Dublin City University) are thanked for their generous access to time correlated single photon counting facilities.

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33 Cross-correlated: the lifetime of the process is less than the FWHM of the excitation pulse.
34 HPLC separation of pipSpip **11** was performed on an Alltech Econosphere Silica 10 μm column using *n*-heptane–2-propanol 95 : 5 and a flow of 1.0 ml min^{-1}. The retention times for the open and closed form were 29.4 and 32.3 min, respectively. The PSS was determined at $\lambda =$ 304 nm, an isoabsorptive point for both forms.
35 The sharp features between $\lambda = 450$ and 500 nm are instrumental artifacts; the spectra are uncorrected for variations in lamp output intensity.
36 The feature at $\lambda \sim 600$ nm is caused by sensitivity of the perylene unit to solvent polarity. Cooling freezes out residual water present in the CH_2Cl_2, thereby decreasing solvent polarity and causing a small shift in the perylene absorption after the second measurement, which as a result causes this spectral distortion.
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