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Energy Transfer

Using a Photoacid Generator to Switch the Direction of Electronic Energy Transfer in a Molecular Triad[**]

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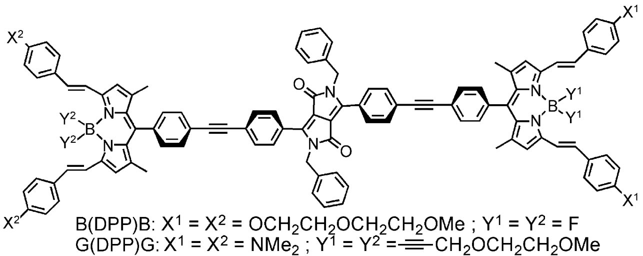
Over the past decade there has been a renaissance of interest in the processes by which electronic energy can be transported around an organized molecular array with minimal loss.[1] The motivation for this research stems from a desire to apply, at a molecular level, the lessons acquired from our ever-deepening understanding of the natural light-harvesting machinery[2] that powers bacterial and green-plant photosynthesis and other biological processes.[3] A key requirement of all such functional units is the need to move the photonic energy to a site where chemical reactions are initiated.[4] Paramount to the successful design of artificial prototypes able to operate in this way is the logical positioning of individual units in a way that favors vectorial electronic energy transfer (EET) along the molecular axis[5,6] or by way of some other preferred pathway.[7,8] An obvious, and indeed enviable, extension for these materials is to devise a simple means by which the EET flow can be reversed, while maintaining very high efficiency. Such switching protocols might involve a change in solvent polarity[9] or temperature,[10] coordination of substrates,[11] light-induced conformational exchange,[12] or modulation of the excitation wavelength.[13] Herein, we introduce a new concept for alternating the EET direction. Our approach, which works in both liquid and solid states, uses a photoacid generator (PAG) to trigger the switch.

The target molecule was constructed with a central 1,4-oxo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole unit, DPP, connecting two disparate Bodipy dyes; namely, a blue dye absorbing strongly at 650 nm and a green dye with prominent absorption centered at 695 nm. Note the green dye is readily protonated at the amine sites to give a blue dye that exhibits an absorption maximum at 630 nm. As such, protonation of the green dye is involved in the switching mechanism; this observation in itself is not a new idea but follows from original work by Armaroli et al.[14] A key feature of our design principle requires that the DPP core absorbs and emits at slightly higher energy than either of the termini. An appropriate prototypic compound is B(DPP)G, as shown in Scheme 1. Preparation of this triad involves cross-coupling the bromo function of the DPP unit with the dedicated terminal alkynes B and G in the presence of Pd^0.[15] The corresponding symmetrical controls, B(DPP)B and G(DPP)G, were prepared using a slight excess of the corresponding starting dye B or G, respectively. The mixed dye, B(DPP)G, was prepared by first cross-coupling the blue dye with the central platform and then attaching the green dye in a separate step (Scheme 1). The boron substituents import polarity to assist purification by column chromatography. The peripheral units attached to the Bodipy dyes were selected in order to modulate the optical properties and, in the case of the green dye, to provide the protonation venue. These new dyes are soluble in common organic solvents and give well-defined proton NMR spectra in keeping with the lack of aggregation in solution (see the Supporting Information).



B(DPP)B: $X^1 = X^2 = OCH_2CH_2OCH_2CH_2OMe$; $Y^1 = Y^2 = F$
G(DPP)G: $X^1 = X^2 = NMe_2$; $Y^1 = Y^2 = -\equiv-CH_2OCH_2CH_2OMe$
B(DPP)G: $X^1 = OCH_2CH_2OCH_2CH_2OMe$; $X^2 = NMe_2$;
$Y^1 = F$; $Y^2 = -\equiv-CH_2OCH_2CH_2OMe$

Scheme 1. Molecular formulae of the molecular triads used herein and their respective abbreviations.

The isolated DPP unit is highly fluorescent ($\lambda_{FLU} = 538$ nm) in solution (see the Supporting Information for a summary of the photophysical properties of the isolated dyes); for example in dioxane at 20 °C, the emission quantum yield (Φ_F) is 0.87 and the excited-singlet-state lifetime (τ_S) is 4.9 ns. On selective excitation at 470 nm of the DPP unit present in B(DPP)B, Φ_F falls to 0.001 while τ_S is decreased to 5.7 ps. There is concomitant appearance of strong emission from the blue dye and, on the basis of comparing the excitation and absorption spectra, it is concluded that intramolecular EET is highly efficient (i.e., $P_{EET} = 99.8\,\%$) in this system (see the Supporting Information for full details); the corresponding rate constant, k_{EET}, is $17.5 \times 10^{10}\ s^{-1}$. Indeed, EET is promoted by a moderately high spectral overlap integral ($J_{DA} = 0.00060$ cm) and thermodynamic driving force, although the center-to-center separation distance ($R = 15$ Å) is reasonably high. Similar behavior holds for G(DPP)G in dioxane solution, although the spectral overlap integral is

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decreased ($J_{DA} = 0.00018$ cm) because of the red-shifted absorption profile that is inherent to the green dye; here, $k_{EET} = 4.0 \times 10^{10}\ s^{-1}$ and $P_{EET} = 99.5\,\%$. Spectroscopic measurements indicate that the quenching of DPP fluorescence is entirely due to intramolecular EET. For the asymmetric triad B(DPP)G, selective illumination into DPP results in EET to both the blue ($P_{EET} = 75\,\%$) and green ($P_{EET} = 25\,\%$) termini but is followed by fast ($k_{EET} = 1.0 \times 10^{10}\ s^{-1}$; $P_{EET} = 98\,\%$) EET from the blue dye to the green analogue. This latter step is driven by a high spectral overlap integral ($J_{DA} = 0.00164$ cm), offset by the large spatial isolation ($R = 34$ Å), and ensures that the green dye is the recipient for essentially all photons absorbed by B(DPP)G.

Protonation[16] of the green dye ($\lambda_{MAX} = 695$ nm) in dioxane with gaseous HCl generates a blue dye ($\lambda_{MAX} = 630$ nm) that is an excellent acceptor for photons absorbed by the DPP unit. Thus, for GH$^+$(DPP)GH$^+$, the overlap integral is high ($J_{DA} = 0.00098$ cm) and intramolecular EET is quantitative ($P_{EET} = 100\,\%$; $k_{EET} = 29.5 \times 10^{10}\ s^{-1}$). The protonated dye shows modest fluorescence centered at 642 nm ($\Phi_F = 0.15$; $\tau_S = 3.2$ ns) that overlaps strongly ($J_{DA} = 0.0025$ cm) with absorption by the blue dye. Consequently, selective excitation of the central DPP unit in B(DPP)GH$^+$ leads to highly efficient intramolecular EET to the protonated dye ($P_{EET} = 62\,\%$; $k_{EET} = 22 \times 10^{10}\ s^{-1}$), with a contribution of direct EET to the blue terminus ($P_{EET} = 38\,\%$; $k_{EET} = 14 \times 10^{10}\ s^{-1}$), followed by long-range EET to the blue terminus ($P_{EET} = 98\,\%$; $k_{EET} = 3.1 \times 10^{10}\ s^{-1}$). The net result, as illustrated in Figure 1, is that protonation of the green dye reverses the EET flow without affecting the overall efficiency, which remains extremely high in all cases (see the Supporting Information for details).

Clearly, the manual addition of acid or base to switch the EET direction is unattractive and impractical but it is a demonstration of the generic principle. A logical improvement is to employ a photoacid (or photobase) to create the required proton gradient[17] and, by moving to a polymer matrix, to restrict the spatial distribution of the switching effect. As proof-of-concept, studies were carried out with a conventional photoacid[18] in both solution and solid states; in principle, related studies could be carried out with an appropriate photobase[19] but these were not pursued. In the first instance, a solution of G(DPP)G in dioxane was examined by fluorescence spectroscopy, with excitation at 525 nm, an isosbestic point for the neutral and dicationic species. Emission occurs exclusively from the neutral species and the intensity at 825 nm was measured. The photoacid generator, PAG (Scheme 2), was added and the solution was kept in the dark except for weak excitation at 525 nm. High concentrations (> 5 mg mL^{-1}) of PAG caused fluorescence quenching but this quenching was minimal at low loadings (i.e., 400 μg mL^{-1}). Under the latter conditions, the solution was illuminated for short periods (typically 30 second bursts) at (330 ± 15) nm from a 250 W xenon lamp to activate the photoacid. The liberated acid causes protonation of the green dye as evidenced by the appearance of fluorescence at 645 nm. Indeed, monitoring the ratio of emission intensities at 645 and 825 nm after each illumination period shows complete conversion of G(DPP)G into the corresponding diacid (see the Supporting Information). Addition of triethylamine leads to partial recovery of the fluorescence characteristic of G(DPP)G, although there is an overall loss of approximately 10 %. This decomposition route is most likely due to free radical attack during liberation of the photoacid. Nonetheless, the principle of fluorescence switching by photolysis has been demonstrated.

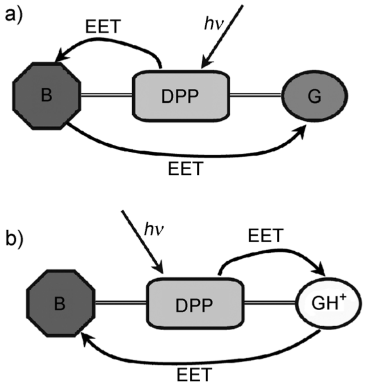
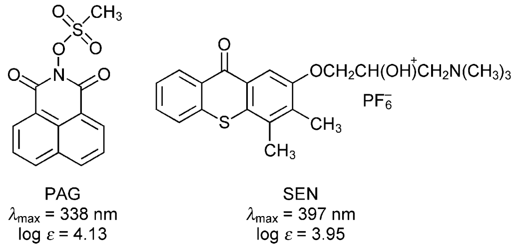


Figure 1. Representation of the chemically modified switching process, in which conversion of G into GH$^+$ causes a change in the direction of electronic energy transfer (EET) from the central donor to the peripheral acceptors.



Scheme 2. Molecular formulae of the photoacid generator (PAG) used to switch the protonation state of the green Bodipy dye and of the oxothioxanthene (SEN) sensitizer employed as UV activator. The spectral absorption properties are given in each case and spectra are shown in the Supporting Information.

A thin (ca. 5 μm) film of poly(methyl methacrylate) (PMMA) was spin-coated onto quartz slides from $CHCl_3$ containing various amounts of B(DPP)G (2–50 μg mL^{-1} initial solution)[20] and dried under vacuum at 40 °C. Fluorescence spectroscopy confirms that EET is highly efficacious in the dried film (see the Supporting Information); fluorescence from DPP is essentially absent, while emission from the blue dye is barely detectable in contrast to strong fluorescence from the green dye. Indeed, the small amount of residual fluorescence from the blue dye becomes quenched at higher loading (> 80 μg mL^{-1} initial solution) of dye because of an intermolecular EET process that does not occur at moderate concentrations in solution. The net result is that only the green dye emits in the film, regardless of the excitation wavelength. At high loading of B(DPP)G, energy migration among molecules of the green dye will disperse the electronic energy since the intermolecular Förster critical distance computed[21] for random orientations of B(DPP)G is approximately 35 Å. On loading the B(DPP)G-doped film (20 μg mL^{-1} initial solution) with PAG (1 mg mL^{-1} of solution prior to spin-coating), the EET step remains unaffected but fluorescence from the green dye is decreased by approximately 40 % relative to a film prepared in the absence of PAG because of intermolecular electron transfer.[23]

Previous work has demonstrated that certain photoacid generators can be activated by two-photon excitation,[24] most notably using high-power lasers emitting in the far-red region.[25] Advantages of this mode of excitation include improved selectivity, depending on the two-photon absorption cross-section of the photoacid precursor,[22] and better spatial resolution.[26] Most photoacid generators can also be activated by sensitization[27] with an added UV absorber. 9-Oxothioxanthones,[28] such as SEN (Scheme 2), are known to function as effective sensitizers for many classes of photoacid generators, including PAG. The main benefit of using a UV absorber to sensitize breakdown of the photoacid is that significantly lower concentrations of PAG become possible, which thereby curtail quenching of fluorescence from the green dye.

Thus, steady-state illumination at 400 nm of a PMMA film containing SEN (2 mg mL^{-1} of initial solution), PAG (200 μg mL^{-1} of initial solution), and G(DPP)G (20 μg mL^{-1} of initial solution) causes progressive replacement of the 725 nm fluorescence with an emission band at 645 nm as protonation of the green dye proceeds. Under such conditions, SEN absorbs more than 95 % of incident near-UV photons. Interestingly, the fluorescence characteristic of SEN is weak relative to that of a PMMA film prepared in the absence of PAG or G because of a combination of electron transfer to PAG and EET to the Bodipy dye (Figure 3). On replacing G with B(DPP)G, the normal fluorescence from the blue dye, which is initially absent, starts to appear as photolysis proceeds (as reported in Figure 2). In this case, there is almost no residual fluorescence from SEN; presumably this is due to an increased rate of EET to the tripartite dye.

Dried films loaded with B(DPP)G, PAG, and SEN as described above could also be activated by two-photon absorption of the sensitizer by excitation with high photon densities delivered at 800 nm. Eliminating either PAG or SEN from the mixture curtailed the characteristic evolution of the fluorescence maximum from 725 to 645 nm. In principle, it should be possible to activate the PAG by two-photon absorption using wavelengths around 700 nm but this could not be realized in practice. An action spectrum recorded for the full mixture, monitoring the ratio of fluorescence intensities at 645 and 825 nm after exposure to a constant photon flux, shows a broad profile with a peak at 800 nm (Figure 4). This observation is consistent with that expected for two-photon excitation of SEN, the absorption maximum of which is at 397 nm.[28] The dimensions of the irradiation area can be varied by changing the microscope objective or by moving to confocal microscopy conditions.

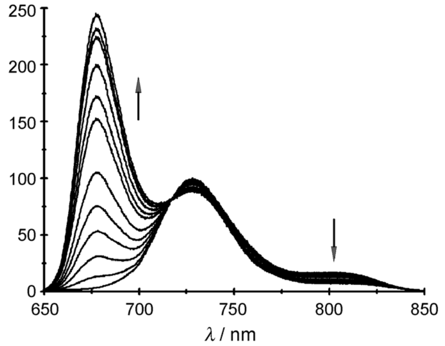


Figure 2. Effect of UV illumination on the fluorescence spectral profile recorded for B(DPP)G in a PMMA film containing PAG (1 mg mL^{-1} initial solution). The excitation wavelength corresponds to an isosbestic point for the blue and green chromophores.

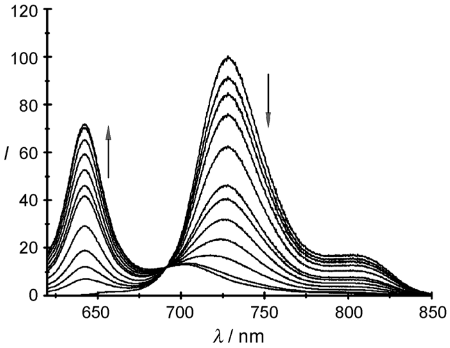


Figure 3. Effect of UV illumination on the fluorescence spectral profile recorded for the green dye (G(DPP)G) in a PMMA matrix loaded with PAG and SEN. Illumination was carried out at 400 nm where SEN is the dominant chromophore.

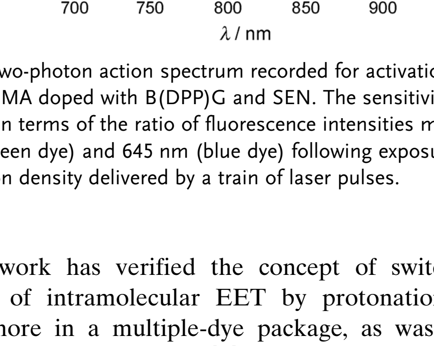


Figure 4. Two-photon action spectrum recorded for activation of the PAG in PMMA doped with B(DPP)G and SEN. The sensitivity is expressed in terms of the ratio of fluorescence intensities measured at 825 nm (green dye) and 645 nm (blue dye) following exposure to a fixed photon density delivered by a train of laser pulses.

This work has verified the concept of switching the direction of intramolecular EET by protonation of one chromophore in a multiple-dye package, as was reported earlier for a molecular dyad.[14] The switch is reversible, at least to a high degree, and can be activated by photochemical means. In the case of B(DPP)G, the state of the switch can be read by fluorescence and/or absorption spectroscopy and activation occurs equally well in solution and in plastic films. Various means of activation are possible and, by using confocal microscopy with two-photon excitation, switching can be restricted to very small zones. In this case, EET might be expected from the blue dye inside the zone to green dye at the periphery of the acidified region. The Förster critical distance computed[21] for such EETs is approximately 30 Å and; with state-of-the-art confocal microscopy, the diameter of the zone could be decreased to approximately 100 nm. The effect of bimolecular EET under such conditions would be a small reduction in the apparent dimensions of the activated zone when measured by fluorescence microscopy. Further modifications of this approach could involve attaching the PAG to the molecular triad so as to minimize the amount of photoacid that needs to be generated. Such protocols could be developed as a means for designing rapid switching systems. We have also shown[16] that green Bodipy-based dyes can be appended to porous microspheres in such a way that reversible protonation still takes place. It is reasonable to suppose that B(DPP)G could likewise be anchored to polystyrene spheres preloaded with PAG. Such materials could be studied at the single-bead level and could be developed as advanced probes for chemical pollutants (e.g., phosgene) and/or acidic contaminants. It should also be emphasized that, while this work has focussed on photoacids, corresponding studies could be conducted with photobases.

Experimental Section

Synthesis and characterization of the new compounds is described in the Supporting Information. All solvents were purchased in spectroscopic grade from Aldrich Chemicals Co., were used as received, and were found to be free of fluorescent impurities. Samples of SEN were obtained from Ward-Blenkinsop Co as the chloride salt and were subjected to ion exchange. Samples of PAG were prepared according to a literature procedure.[26] Absorption spectra were measured with a Hitachi U3310 spectrophotometer and fluorescence spectra were measured with a fully corrected Jobin–Yvon Fluorolog tau-3 spectrometer for quantitative measurements and a Hitachi F-4500 fluorescence spectrometer for routine studies. Steady-state irradiation studies were carried out with the sample solution contained in a quartz cell, after purging with N_2, using a 250 W xenon arc lamp. The light beam was passed through a high radiance monochromator to isolate the required excitation wavelength. The course of reaction was followed by fluorescence spectroscopy. Irradiation studies made with PMMA films, after casting by spin-coating (see the Supporting Information), utilized the same excitation source. For the two-photon excitation studies, a train of 50 pulses delivered from a frequency-doubled Nd–YAG laser (FWHM = 4 ns) was directed to a microscope objective and focused onto the plastic film. The laser beam was passed through an OPA in order to isolate a spectral region centered at approximately 800 nm.

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