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Light Harvesting with Gels

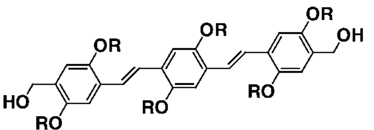
Gelation-Assisted Light Harvesting by Selective Energy Transfer from an Oligo(*p*-phenylenevinylene)-Based Self-Assembly to an Organic Dye**

Ayyappanpillai Ajayaghosh, Subi J. George, and Vakayil K. Praveen*

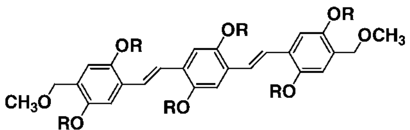
Dedicated to the memory of Darshan Ranganathan

Excitation energy transfer within and between molecular systems plays an important role in natural processes, such as photosynthesis. In this context, there has been widespread interest in mimicking the mechanism of solar-energy harvesting of natural photosynthesis with the aid of synthetic molecular systems. Apart from this, photoinduced energy transfer has become significant in the area of photovoltaics, organic light-emitting diodes, fluorescent labeling, and in a variety of photonic devices. In most of these cases, energy transfer is considerably influenced by the supramolecular ordering and spatial relationship of the donor and acceptor chromophores. Molecular architectures such as hydrogen-bonded systems,[1] dendrimers,[2] chromophore-linked polymers,[3] Langmuir–Blodgett films,[4] and self-assembled monolayers[5] are of extremely important in this context. Among a plethora of donor–acceptor systems investigated, energy and electron transfer from oligo(phenylenevinylene)s (OPVs) and poly(phenylenevinylene)s (PPVs) to acceptors, such as C_{60},[6] phenanthroline,[7] and doped organic dyes[8] have generated enormous interest because of their potential use in photovoltaic and light-emitting devices. From this view point, the recent reports by Meijer and coworkers on energy and electron transfer from OPV-functionalized dendrimers and supramolecular assemblies to various acceptors are of particular interest.[9] This situation has prompted us to investigate on the potential of OPV based organogels for the purpose of energy transfer and light harvesting.[10]

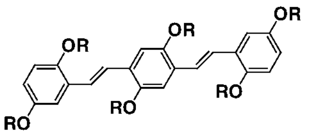
Small-molecule-based organogels have attracted much attention in recent years because of their interesting physical properties and architectural elegance.[11] However, organogels based on π-conjugated systems are relatively very few.[12] Recently, we have reported hydrogen-bond- and π-stack-induced supramolecular assembly of the OPV derivatives **1a**,**b**, which leads to the formation of entangled nanostructures, which induce gelation of hydrocarbon solvents.[13] The absorption and emission properties of **1a**,**b** showed dramatic changes during gelation, which is an indication of strong intermolecular π-electronic coupling of the ordered self-assembled OPV gel. Excitation of **1a**,**b** in cyclohexane at 380 and 470 nm revealed the emission corresponding to the monomeric species (λ_{em} = 455 and 483 nm, $\Phi_f = 0.40 \pm 0.01$ related to quinine sulfate, $\tau = 1.46$ ns; Figure 1, spectrum b) and self-assembled species (λ_{em} = 525 and 565 nm, $\Phi_f = 0.40 \pm 0.01$ related to Rhodamine 6G, $\tau = 1.62$ ns; Figure 1, spectrum c), which showed strong dependency on solvent polarity and temperature.



1a,b

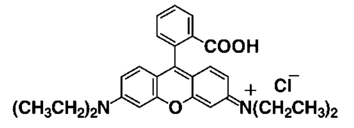


2a,b



3a,b

a: R = $C_{12}H_{25}$
b: R = $C_{16}H_{33}$



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Herein we describe an interesting case of a thermoreversible fluorescence-resonance energy transfer (FRET) and light harvesting, exclusively from OPV based supramolecular gel nanostructures of **1a**,**b** to an organic dye. To study the feasibility of such an energy transfer, we chose Rhodamine B as the acceptor, the absorption (λ_{max} = 555 nm) of which

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[*] Dr. A. Ajayaghosh, S. J. George, V. K. Praveen
Photochemistry Research Unit
Regional Research Laboratory, CSIR
Trivandrum-695019 (India)
Fax: (+91) 471-490-186
E-mail: aajayaghosh@rediffmail.com

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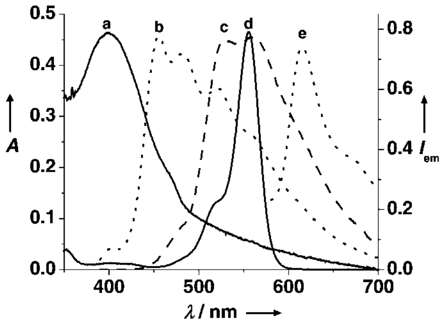

Figure 1. Individual absorption and emission spectra of **1b** and Rhodamine B in cyclohexane:chloroform (16:1). a) Absorption of **1b**, b) emission of monomeric **1b** at 380 nm excitation, c) emission of self-assembled **1b** gel at 470 nm excitation, d) absorption of Rhodamine B, e) emission of Rhodamine B (λ_{ex} = 535 nm).

matches with the emission of the self-assembled OPV (λ_{em} = 527 and 560 nm) as indicated by their individual absorption and emission spectra (Figure 1). The absorption spectrum of a mixture of **1b** (1.01×10^{-5} M) and Rhodamine B (8×10^{-5} M) in a mixture of cyclohexane and chloroform (16:1) was recorded, which showed the characteristic absorption bands of the individual components, thereby ruling out any ground-state interaction between them.

In Figure 2a, the fluorescence emission spectra of **1b** and a mixture of **1b** and Rhodamine B in cyclohexane:chloroform (16:1) are shown. In this solvent mixture, **1b** (1.01×10^{-5} M) has a broad emission with three emission maxima at 455, 483, and 525 nm with a shoulder around 565 nm. When excited at 380 nm in the presence of Rhodamine B (8×10^{-5} M), selective quenching of the emission between 500–650 nm, corresponding to the self-assembled OPV, could be seen with the concomitant emission of Rhodamine B at 620 nm. This result is an indication of excitation energy-transfer selectively from the self-assembled OPVs to the Rhodamine B. The emission between 400–480 nm of the dissolved molecular OPV was virtually unaffected indicating no energy transfer from them. When the same solution was excited at 470 nm, the emission maxima at 527 and 560 nm corresponding to the self-assembled species were significantly quenched and the dye emission occurred at 620 nm (Figure 2b). When an optically matching solution of the dye was excited at 380 or 470 nm in the absence of **1b**, no significant emission could be seen. This situation is a clear indication that the emission from the dye occurs as a result of the energy transfer from the self-assembled gel and not by direct excitation. While, the emission profile of the optically matching solutions of the dye upon direct excitation at 535 nm and indirect excitation in the presence of **1b** at 470 nm were perfectly matching, the intensity of the latter was higher (inset of Figure 2b). This amplified emission points towards the efficient energy hopping from the donor to the acceptor by a Förster type mechanism.[14] The rate of energy transfer k_{ET} ($1.67 \times 10^{13}\,\text{M}^{-1}\text{s}^{-1}$) was estimated from the rate of fluorescence quenching k_{SV} ($2.7 \times 10^{4}\,\text{M}^{-1}$) obtained from the Stern–Volmer plot and the lifetime of the self-assembled species (τ = 1.62 ns).

Efficient energy transfer in solid film is a prerequisite for the designing of light-harvesting devices. In this context, we were keen to study the emission profile of a xerogel film of **1b** containing Rhodamine B (2:1 mol ratio). Interestingly, energy transfer occurs with high efficiency in this case (Figure 3). Emission maximum of the OPV film at 550 nm was completely quenched with the formation of a strong fluorescence from the dye (λ_{max} = 620 nm), when excited at 380 nm. However, emission of the same film upon direct excitation of the dye at 535 nm was negligible reiterating an efficient energy transfer in the former case. The apparent efficiency of energy transfer as estimated from the OPV fluorescence-

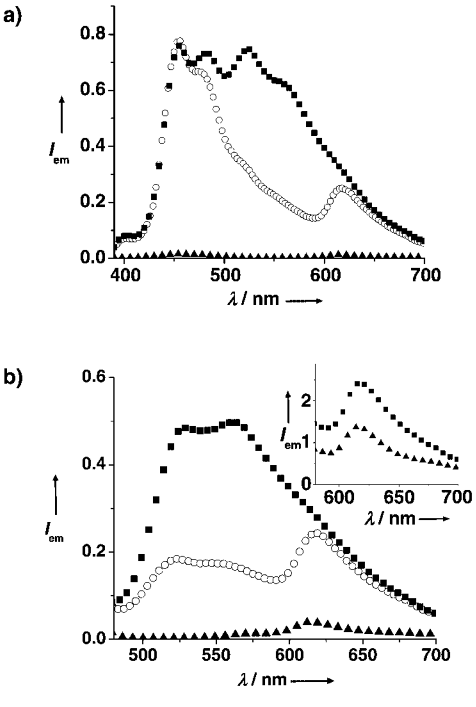

Figure 2. Energy-transfer quenching of the fluorescence of **1b** (1.01×10^{-5} M) in cyclohexane:chloroform (16:1) in the presence of Rhodamine B (8×10^{-5} M) a) at an excitation wavelength of 380 nm and b) at 470 nm. (■) fluorescence of **1b**, (○) fluorescence of **1b** + Rhodamine B, (▲) fluorescence of Rhodamine B. Inset of Figure 2b shows the emission of the dye on its indirect excitation at 470 nm (■) and direct (▲) excitation at and 535 nm illustrating the amplified emission.

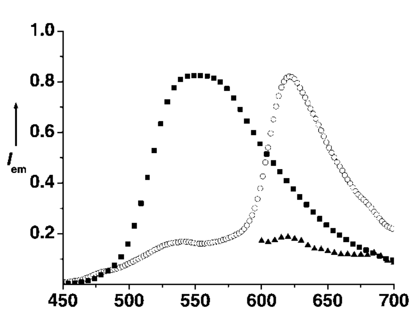

Figure 3. Normalized emission (λ_{ex} = 380 nm) from the film of **1b** (■), film of **1b** + Rhodamine B (2:1 mol ratio; ○), and from direct excitation (λ_{ex} = 535 nm) of Rhodamine B (▲), which illustrates the amplified emission from Rhodamine B by energy transfer.

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quenching profiles was 90 % for the xerogel film and 63 % for the solution. In the former case, most of the OPVs are in the form of self-assembled xerogel, where the donor and the acceptor chromophores are present well within the Förster radius, thereby facilitating efficient excitation-energy hopping when compared to that in solution. The observed emission from Rhodamine B as a result of the energy transfer from the OPV xerogel was several times more intense than that resulting from the direct excitation of the dye, which indicates efficient light harvesting in this donor–acceptor system.[15]

The role of the gel self-assembly in promoting the energy transfer is established by the temperature-dependent emission studies (Figure 4). At 5 °C, more than 90 % of the OPVs exist in the self-assembled form as evident from the emission spectrum. When excited at 380 nm, in the presence of the dye at 5 °C, the emission of the gel was quenched and the dye emission occurred at 620 nm. Upon heating, the emission from the dye at 620 nm was decreased (> 90 % quenching above T_{gel}) with the concomitant increase of the molecular OPV emission at 455 and 483 nm (Figure 4, inset). Upon cooling the solution, the dye emission is regained. Since the energy transfer between the donor and acceptor is usually independent of temperature, the observed temperature effect in energy transfer is the consequence of thermoreversible breaking and forming of the self-assembled gel nanostructures. Similar results were obtained for the OPV **1a**. Interestingly, energy transfer was not predominant in the case of **2a**,**b** and **3a**,**b**, which failed to form gels (See Supporting Information).

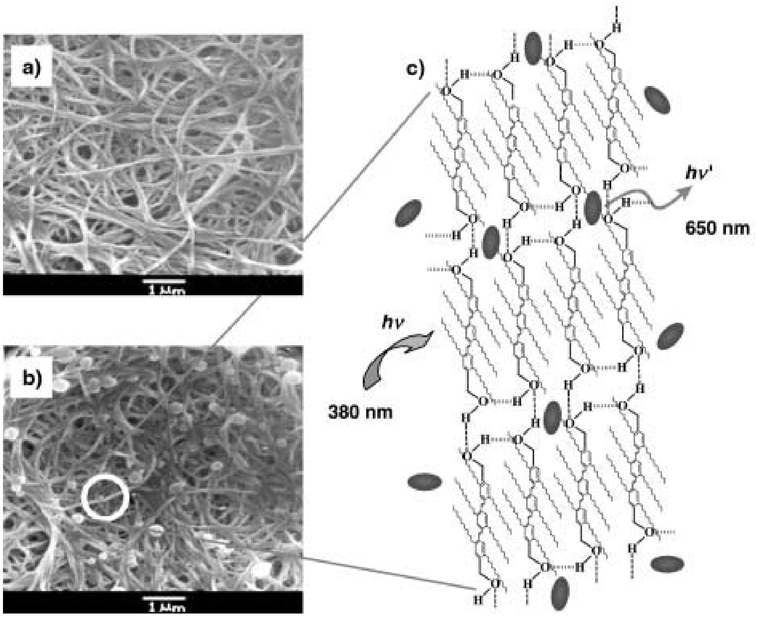

Figure 5. SEM images of the gel of **1b** from cyclohexane:chloroform (16:1) in the a) absence of Rhodamine B, and b) presence of Rhodamine B. c) Probable self-assembly of Rhodamine B dispersed OPV gel, the ellipsoids represent the trapped Rhodamine B molecules.

Supramolecular organization of the donor chromophore (OPV) has a crucial role in transferring the excitation energy to the dispersed Rhodamine B (Figure 5). Detailed morphological studies of the OPV gels in the absence and presence of Rhodamine B using scanning electron microscopy (SEM) show that the dye molecules are partly trapped in the OPV-gel nanostructures and partly remain in the solvent medium. The energy transfer preferably occurs to the gel-trapped dye molecules, which are within the Förster radii. This may be the reason why we had to use excess concentrations of the dye relative to the OPVs for better energy transfer in the solvent medium. On the other hand, efficient fluorescence quenching and energy harvesting is possible from OPV xerogel film with lesser amount of the dye, since majority of the dye molecules are trapped in the xerogel film.

In conclusion, the role of hydrogen-bonded and π-stacked OPV self-assembly in facilitating energy transfer and light harvesting, exclusively from the gel phase is demonstrated. More importantly, the energy transfer could be thermally controlled by the reversible gelation of the OPVs. Detailed study of the role of the OPV gel morphology on energy and electron transfer to various acceptors and their use in photovoltaic devices are in progress.

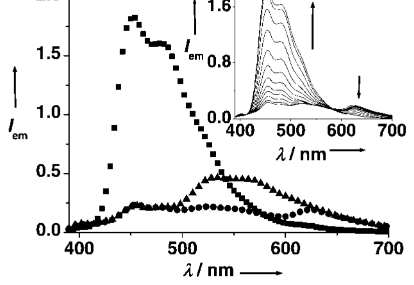

Figure 4. Temperature-dependence of energy transfer between **1b** (1.05×10^{-5} M) and Rhodamine B (5.85×10^{-5} M). (▲) emission spectrum of **1b** at 5 °C, (●) emission spectrum of **1b** + Rhodamine B at 5 °C, (■) emission spectrum of **1b** + Rhodamine B at 40 °C. Inset shows the decrease in Rhodamine B emission with increasing temperature from 5 °C to 40 °C.

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Photochemotherapeutical Drugs

Nucleotide Cross-Linking Induced by Photoreactions of Platinum(IV)–Azide Complexes**

Philippe Müller, Björn Schröder,
John A. Parkinson, Nicole A. Kratochwil,
Robert A. Coxall, Andrew Parkin, Simon Parsons,
*and Peter J. Sadler**

State-of-the-art lasers and fibre optics now have the ability to reach any tissue in the body. A site-specific activation of photochemotherapeutic agents is therefore possible, which minimizes the severe side-effects of chemotherapy. Photosensitizers which catalyze the production of singlet oxygen are used in clinics for photodynamic therapy.[1] This technique relies on the presence of oxygen in the target tissue. A new approach towards the development of oxygen-independent photochemotherapeutic agents has recently been developed.[2–4] Photoactive Pt^{IV} analogues of the anticancer drug cisplatin (*cis*-[Pt^{II}Cl$_2$(NH$_3$)$_2$]) are of special interest: it has been shown that nucleotide platination by Pt^{IV}–diiododiamine compounds can be induced by visible light.[4] However, slow photoreactions and low stability against biological reducing agents such as glutathione can be a problem with this class of complexes. We have therefore sought alternative Pt^{IV} compounds that are better suited to this purpose, especially those more stable towards reducing agents.[5]

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[*] Prof. Dr. P. J. Sadler, P. Müller, B. Schröder, J. A. Parkinson,
N. A. Kratochwil, R. A. Coxall, A. Parkin, S. Parsons
Department of Chemistry
The University of Edinburgh, King's Buildings
West Mains Road, Edinburgh EH9 3JJ (UK)
Fax: (+44) 131-650-6452
E-mail: p.j.sadler@ed.ac.uk

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