Energy Transfer

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Molecular Wire Encapsulated into π Organogels: Efficient Supramolecular Light-Harvesting Antennae with Color-Tunable Emission**

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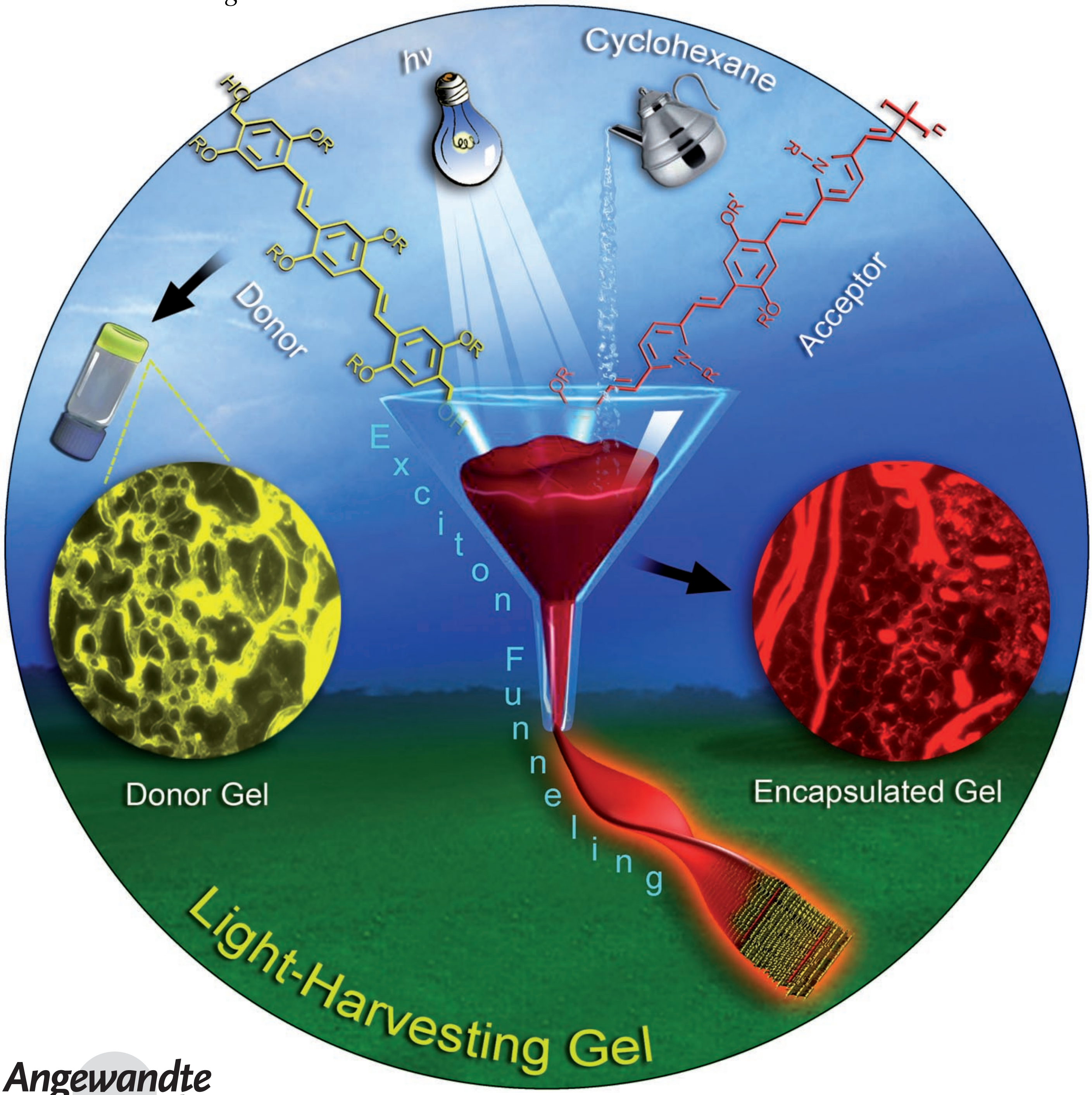
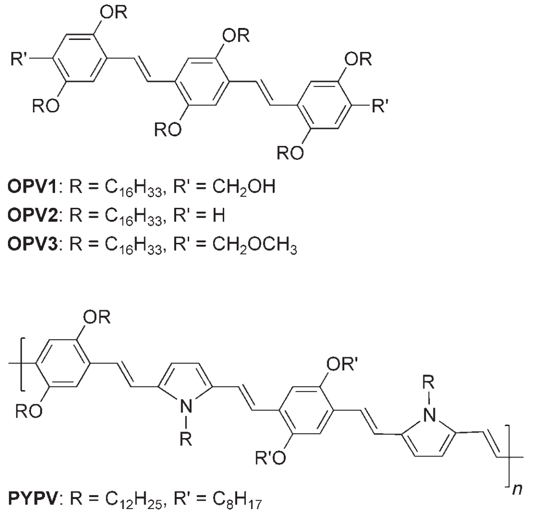


In natural light-harvesting (LH) assemblies, the light-absorbing chromophores are organized in a specific geometry and encapsulated within the soft gel-like biological tissues. Fast directional migration of excitation energy within the chromophore assemblies before being transferred to the reaction center is crucial to the LH process.[1] The fascination of the architecture and mechanism by which such systems operate has been the driving force to mimic natural LH systems with artificial molecular assemblies.[2–5] Research in this direction is further driven by the recent developments in the area of advanced materials, particularly in the design of optoelectronic devices, where energy- and electron-transport processes over a few nanometers are crucial.[2d,5,6] The supramolecular chemistry of functional dyes and π-conjugated molecules has been playing a significant role in the above developments.[7]

Organogels are excellent media to facilitate energy-transfer processes.[8–10] The choice of a donor and an acceptor with suitable optical and self-assembly properties is extremely important in the design of an organogel-based light-harvesting assembly. Extensive studies by Meijer and co-workers have revealed that self-assembled oligo(*p*-phenylenevinylene)s (OPVs) are efficient excitation energy donors to suitable acceptors.[11] In a series of studies we have demonstrated that suitably functionalized OPVs can form luminescent π organogelators with supramolecular architectures of different sizes and shapes as well as with distinct optical properties.[12] By combining these properties of OPVs, we have shown earlier that energy transfer can occur from OPV gels to entrapped acceptors.[10] In these cases, a large number of acceptors were needed for efficient energy transfer. Therefore, the challenge is to identify a suitable acceptor that traps the excitation energy through an efficient antenna effect when encapsulated in extremely small quantities within a donor gel scaffold. Herein we show that the encapsulation of less than 2 mol% **PYPV** (Scheme 1) within the organogel scaffold of OPVs facilitate fast exciton funneling and efficient energy transfer which results in a supramolecular light-harvesting antenna. Although a variety of organic dyes and chromophores have been reported as acceptors, this is the first use of a molecular wire for trapping excitation energy in an organogel medium.[13]



Scheme 1. Molecular structures of the OPV donors (**OPV1–3**) and the **PYPV** acceptor.

We have chosen three OPV derivatives as energy donors (Scheme 1). **OPV1** forms strong gels and **OPV2** forms weak gels in cyclohexane whereas **OPV3** is a non-gelling molecule.[12c] The acceptor **PYPV** has an average molecular weight (M_n) of approximately 4358 $\mathrm{g\,mol^{-1}}$ with a polydispersity index of 1.12. **OPV1** exhibits an absorption maximum around 407 nm and an emission maximum at 463 nm in chloroform (1×10^{-5} M). However, in cyclohexane (1×10^{-5} M), the absorption spectrum exhibits an additional shoulder at 468 nm and the emission maximum is shifted to a longer wavelength; this is a thermoreversible process.[12c] These spectral shifts are associated with the aggregation of OPV molecules in cyclohexane. At 4×10^{-4} M, **OPV1** forms a gel in cyclohexane.[14] As a result, the emission maximum of the molecule is completely shifted in favor of the aggregates.[15]

A solution of **PYPV** (6.12×10^{-6} M) in cyclohexane showed a broad absorption band with a maximum around 512 nm and an emission maximum at 584 nm. The emission of the self-assembled donor overlaps the absorption band of the acceptor (spectral overlap integral $J(\lambda)$: $5.83\times10^{15}\,\mathrm{M^{-1}\,cm^{-1}\,nm^4}$) which indicates the possible transfer of resonant excitation energy by nonradiative dipole–dipole coupling. The well-separated absorption maxima of the donor and the acceptor, the good overlap between the emission band of the donor and the absorption band of the acceptor, and the large extinction coefficient of the acceptor are favorable for the transfer of energy between the two. A comparison of the absorption spectra of the individual donor and the acceptor compounds with that of a mixture of both at the required concentrations reveals that the possibility of direct excitation of the acceptor is minimal at the excitation wavelength of the donor.[15]

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The feasibility of energy transfer between **OPV1** and **PYPV** has been studied in the gel state by encapsulation of the latter within the self-assembled structure of the former. Small quantities of **PYPV** (0–1.53 mol %) were dissolved in a solution of **OPV1** in cyclohexane (1.12 mM) by heating to 70 °C. The solution was cooled and kept under room temperature to form a self-supporting gel. The addition of 1.53 mol % **PYPV** resulted in the gel stability being marginally decreased, as indicated by a 10 °C lowering of the gel melting temperature (T_{gel}) from 70 to 60 °C. Moreover, the absorption band of the **PYPV** in the gel state is red-shifted, which may be due to the increase in the effective conjugation length upon encapsulation.[15] The scanning electron microscopy (SEM) and atomic force microscopy (AFM) analyses of the gel before and after the addition of **PYPV** revealed that the encapsulation of the molecular wire did not induce any significant changes to the morphology of the self-assembled structure.[15]

Fluorescence microscopy images of gel (1.12 mM) fibers upon illumination with UV light (340–380 nm) show bright yellow emission (Figure 1 a) which turns red upon encapsulation of 1.53 mol % **PYPV** (Figure 1 b). Such a dramatic color change in the emission of the gel fibers upon excitation of **OPV1** with a low loading of **PYPV** could be attributed to efficient energy transfer to the latter. A schematic representation of the plausible self-assembled structure of the donor and the acceptor molecules is shown in Figure 1 c. This representation is in analogy with our earlier findings on the self-assembly of OPVs in the gel state.[12c] The fluorescence emission of **OPV1** before and after encapsulation of **PYPV** is shown in Figure 2 a. The emission intensity of the **OPV1** gel at 537 nm exhibited a sharp decrease, with the concomitant formation of a red emission at 622 nm upon excitation at 380 nm. The emission of the **OPV1** gel at 537 nm exhibited an approximately 95 % quenching when the **PYPV** concentration reached 1.53 mol %. Direct excitation of **PYPV** (1.53 mol %) at 380 nm in cyclohexane in the absence of **OPV1** resulted in a negligible emission. Further studies were thus performed to confirm that the enhanced emission from **PYPV** in the presence of **OPV1** gel is the result of energy transfer and does not arise from the restricted environment of the gel medium. When the encapsulated **PYPV** was directly excited at 530 nm in the donor gel, the resultant emission spectrum resembled that obtained on excitation at 380 nm, but was less intense (Figure 2 b). On the other hand, when **PYPV** alone in cyclohexane was excited at 530 nm, the resultant emission spectrum was blue-shifted and had almost the same intensity as that of the spectrum obtained in the gel state upon excitation at 530 nm (Figure 2 b). These observations strongly support the fact that the enhanced emission from the encapsulated **PYPV** in the gel is due to energy transfer.[16] The 38-nm red-shift in the emission band of the encapsulated **PYPV** in cyclohexane relative to that in the absence of **OPV1** ($\lambda_{ex} = 380$ nm or 530 nm), could be due to the planarization of the former in the constrained gel medium, thereby leading to an increase in the effective conjugation length—which is also apparent from the shift in the absorption maximum.

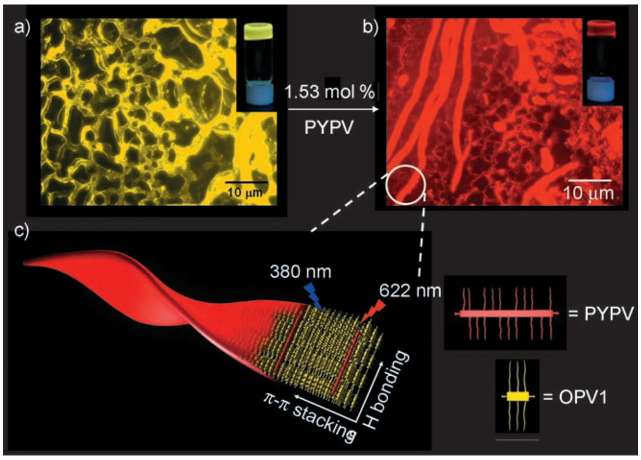

Figure 1. Fluorescence microscopy images of the drop-casted **OPV1**-cyclohexane gel (1.12 mM): a) in the absence and b) presence of **PYPV** (1.53 mol%), the insets show photographs of the gels under the respective conditions when illuminated at 365 nm. c) A schematic representation of a **PYPV**-encapsulated **OPV1** tape.

The fluorescence decay profiles of **OPV1** gel in cyclohexane (probed at 537 nm) in the presence of different amounts of **PYPV** are shown in Figure 2 c. In the absence of **PYPV**, the **OPV1** gel exhibited a biexponential decay with time constants $\tau_1 = 1.62$ ns (49 %) and $\tau_2 = 4.43$ ns (51 %), whereas the emission decay of **OPV1** becomes faster with an increasing concentration of **PYPV**. In the presence of 1.53 mol % **PYPV**, **OPV1** exhibited a fast biexponential decay with time constants of $\tau_1 = 0.72$ ns (56 %) and $\tau_2 = 2.22$ ns (44 %). Such a progressive shortening of the emission decay time of the donor in the presence of an acceptor indicates nonradiative energy transfer and rules out the possibility of trivial radiative energy transfer (emission-reabsorption) mechanism.[11c,17] Further evidence for the transfer of excitation energy is obtained from the temporal rise in the emission of **PYPV** when excited at 375 nm in the gel phase (Figure 2 c, inset).

Energy transfer is found to be more efficient in the gel state than in solution, and is strongly influenced by solvents. This is clear from Figure 2 d, in which the plot of the relative fluorescence intensities against the molar ratio of **PYPV** and **OPV1** in the gel state is compared with those in cyclohexane and chloroform solutions. Similarly, the energy-transfer efficiencies of the weakly gelling **OPV2** and the non-geling **OPV3** in cyclohexane are extremely low, as indicated from the fluorescence emission studies in the presence of **PYPV**.[15] On the basis of these observations, the high-energy transfer efficiency of the **OPV1** gel (95 % as calculated from the fluorescence-quenching data) at a very low concentration of **PYPV** (1.53 mol %) is attributed to fast exciton migration along the self-assembled tapes.

Insight into the exciton migration between **OPV1** aggregates within the gel scaffold was obtained by time-resolved anisotropy measurements.[15] The two predominant pathways for the loss of anisotropy of organized donors are either by rotational motion or by energy migration.[18] In the case of the self-assembled **OPV1** gel, fluorescence depolarization by rotational motion is less favored and hence energy migration

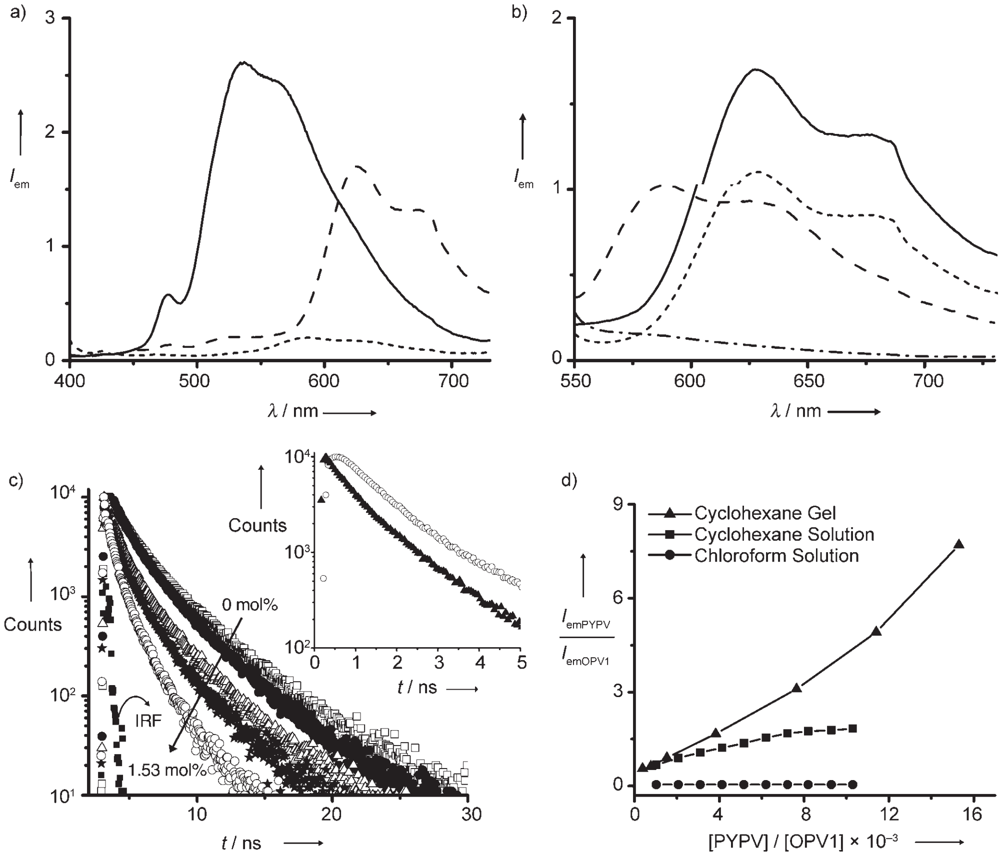

Figure 2. a) Fluorescence spectrum of the **OPV1**-cyclohexane gel (4×10^{-4} M, $l=1$ mm) in the absence (——) and in the presence (– – –) of 1.53 mol% **PYPV** ($\lambda_{ex}=380$ nm). The fluorescence spectrum of **PYPV** alone (-----) in cyclohexane upon excitation at 380 nm is shown for comparison. b) Comparison of the fluorescence spectrum of **PYPV** (1.53 mol%) in the **OPV1**-cyclohexane gel when excited at 380 nm (——) and at 530 nm (-----); **PYPV** in cyclohexane upon excitation at 530 nm (– – –); and the **OPV1**-cyclohexane gel upon excitation at 530 nm (–•–•). c) Fluorescence decay profiles of the **OPV1**-cyclohexane gel (4×10^{-4} M, $l=1$ mm) at various concentrations of **PYPV** (0–1.53 mol%), monitored at 537 nm. The inset shows the decay profiles of **PYPV** (1.53 mol%) in the **OPV1**-cyclohexane gel (○; $\lambda_{ex}=375$ nm) and **PYPV** alone (▲), monitored at 680 nm. IRF = instrument response function. d) Plots of the relative fluorescence intensities against the molar ratio of **PYPV** and **OPV1** under different conditions.

is the feasible pathway.[8a,18d] Exciton migration within **OPV1** aggregates leads to a loss of the memory of the initial excitation polarization, which eventually results in almost equal intensities of the emitted light that is polarized either parallel ($I_{\parallel}$) or perpendicular ($I_{\perp}$) to that of the excitation source. A gel of the **OPV1** in cyclohexane (4×10^{-4} M) exhibited an initial anisotropy value (r_0) of 0.32 with a decay time $\tau_r=78$ ps which rapidly loses the anisotropy memory and reaches a plateau at $r_\infty=0.04$.[15] The anisotropy decay time τ_r gives an estimate of the rate of energy migration (k_{EM}) from the higher to the lower energy state, and is found to be 1.28×10^{10} s^{-1}. The extremely fast fluorescence depolarization is an indication of the fast interchromophore migration of a singlet exciton,[18] which facilitates efficient energy funneling to a suitable acceptor.

The time-resolved emission spectra (TRES) of the **OPV1** gel in cyclohexane (4×10^{-4} M) recorded at different times after excitation at 375 nm are shown in Figure 3a. At short times, the recombination of excitons exhibited a broad emission band with a shoulder in the shorter wavelength region. With an increase in time after excitation, the intensity of the shoulder bands in the shorter wavelength region is decreased and there is a red-shift of the emission. The spectrum obtained after 336 ps was almost identical to the steady-state emission of the **OPV1** gel. The rapid decay of the higher energy shoulder bands and the dynamic red-shift of the emission within short time periods are attributed to fast exciton migration from low-order aggregates (higher energy sites) to higher order aggregates (lower energy sites) of the **OPV1** gel.[18c,19]

The wavelength dependence of the emission decay of **OPV1** in the gel state provides further evidence for energy migration (Figure 3b). The emission at 478 nm decays faster than the higher wavelength (lower energy) emission, and contains a fast decay component (79 ps). The lifetime decay monitored at 536 nm is apparently biexponential, whereas the decay monitored at 574 nm emission is found to be multiexponential with a growth component of 100 ps. Such delayed growth (Figure 3b, inset) within the initial short time periods indicates migration of exctions from the higher to the lower energy sites and the population of the excited states of the latter.[18c,20]

An interesting feature of the present light-harvesting system is the temperature dependency of the energy-transfer

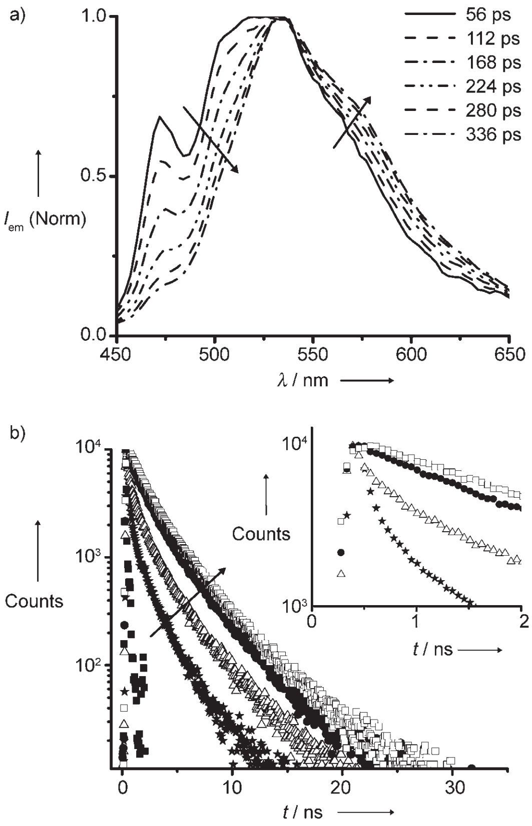

Figure 3. a) Time-resolved emission spectra of the **OPV1** gel. b) Emission decay curves of the **OPV1** gel monitored at different wavelengths. The inset shows the initial growth in the emission decay of the **OPV1** gel after short time periods, as monitored at different wavelengths after excitation. IRF: ■, 478 nm: ★, 504 nm: △, 536 nm: ◆, 574 nm: □. In all experiments [**OPV1**] = 4×10^{-4} M in cyclohexane, l = 1 mm, λ_{ex} = 375 nm.

efficiency and the consequent change in the emission color (Figure 4). Excitation of the **OPV1** gel containing **PYPV** (1.53 mol%) in cyclohexane (4×10^{-4} M) at 10 °C resulted in a red fluorescence at 622 nm. Interestingly, the intensity of the emission at 622 nm decreased as the temperature was increased, and a broad emission between 440 nm to 700 nm formed. Surprisingly, a white emission was visible at 54 °C, which upon further heating changed to blue ($\lambda_{em} = 454$ nm). The self-assembly partially breaks into aggregates and single molecules between 50 and 60 °C. Energy transfer occurs partly to the molecular wire, thus resulting in a red emission and the residual green emission from the self-assembled species together with the blue emission of the single molecules. This situation leads to the presence of the fundamental RGB emission that leads to white light when excited at 365 nm. Thus, with an increase in temperature, the red emission changes to white and then blue in a reversible fashion, similar to a temperature-sensitive supramolecular chameleon.

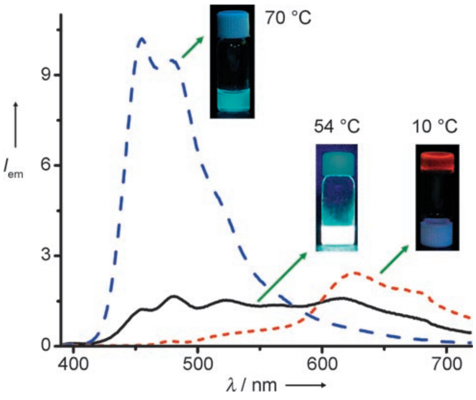

Figure 4. Temperature-dependence of the energy transfer between **OPV1** (4×10^{-4} M) and **PYPV** (1.53 mol%) in a cyclohexane gel (l = 1 mm, λ_{ex} = 380 nm). The emission spectra were recorded at 10 °C (----), 54 °C (——), and 70 °C (– – –). The inset shows the corresponding emission color under illumination at 365 nm.

In conclusion, we have demonstrated the design of a novel organic supramolecular light-harvesting antenna by encapsulating an energy-accepting molecular wire into an energy-donating π-gel scaffold. This could be the first example in which a semiconducting molecular wire has been used as an energy trap in the design of a light-harvesting gel. Energy transfer is feasible only in the case of the gel and occurs exclusively from the donor (OPV) self-assembled structure to the molecular wires as a result of fast and efficient exciton migration. These results are expected to open up further research interests in the design of artificial light-harvesting assemblies.

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[13] During the revision of this manuscript an interesting study was reported which pertains to a new approach to light harvesting by π-conjugated wires encapsulated in a shape-persistent macrocycle through covalent linkages. However, this approach is different from our work described here. For details see: K. Becker, P. G. Lagoudakis, G. Gaefke, S. Höeger, J. M. Lupton, *Angew. Chem.* **2007**, *119*, 3520–3525; *Angew. Chem. Int. Ed.* **2007**, *46*, 3450–3455.

[14] In cyclohexane, the minimum concentration required for the gelation of **OPV1** in a 1-mm cuvette (4×10^{-4} M) is much lower than that in a 1-cm cuvette or vial (1.12 mM).

[15] See the Supporting Information.

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