Energy Transfer in Supramolecular Assemblies of Oligo(*p*-phenylene vinylene)s Terminated Poly(propylene imine) Dendrimers

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Abstract: Poly(propylene imine) dendrimers have been functionalized with π-conjugated oligo(*p*-phenylene vinylene)s (OPV's) through an amide linkage and are fully characterized. In solution the dendrimers behave as globular entities without specific interactions between the OPV units. The OPV dendrimers have an amphiphilic nature and self-assemble at the air−water interface forming stable monolayers in which the dendritic surfactants presumably adopt a cylindrical shape; all the OPV's are aligned perpendicular to the water surface, and the dendritic poly(propylene imine) cores face the aqueous phase. Optical spectra taken from Langmuir−Blodgett films show a small blue shift indicative of interactions between the OPV units. Spin-coated homogeneous thin films could be obtained from solutions containing dendrimers loaded with dyes. The optical properties of these films are similar to the Langmuir−Blodgett films which points to the same type of organization of the OPV's. The OPV dendrimers are effective extractants of anionic dye molecules from water to organic solvents. Ratios between dye and dendrimer can be easily tuned by varying the concentration of dye in the water layer. The host−guest assemblies show not complete energy transfer from the OPV units to the encapsulated dye molecules in solution. The energy transfer is very efficient in spin-coated films of dendrimer/dye assemblies and the emission wavelength can be adjusted by using a variety of dye molecules. The dendrimer/dye systems mix very well with poly(*p*-phenylene vinylene)s (PPV's) forming good quality thin films in contrast to films obtained from dye/PPV without dendrimer. The OPV units in the dendrimer act as a compatibilizer in these systems and energy transfer is observed from the organic PPV polymer to the dye. It gives the possibility of tuning the emission wavelength of the PPV thin films by using the appropriate encapsulated dye.

Introduction

Dendrimers are well-defined, hyperbranched macromolecules with a high concentration of peripheral chain ends.[1] Many of the properties of these molecules are strongly influenced by these endgroups. Poly(propylene imine) dendrimers terminated with fatty acids, for example, behave like inverted unimolecular dendritic micelles that consist of a polar core and an apolar periphery.[2] The ambivalent nature of these dendrimers can be used to self-assemble them at air−water interfaces and in water[3] or to solubilize hydrophilic dye molecules in apolar media.[4,5]

Dendrimers with semiconducting π-conjugated systems as their core have become the subject of intense research the last two years with the main goal of obtaining isolated soluble wires resulting in high fluorescence quantum efficiencies.[6] π-Conjugated oligomers attached to the periphery of dendrimers are, however, remarkably rare.[7−9] These dendritic macromolecules are of interest because they give highly amorphous thin films

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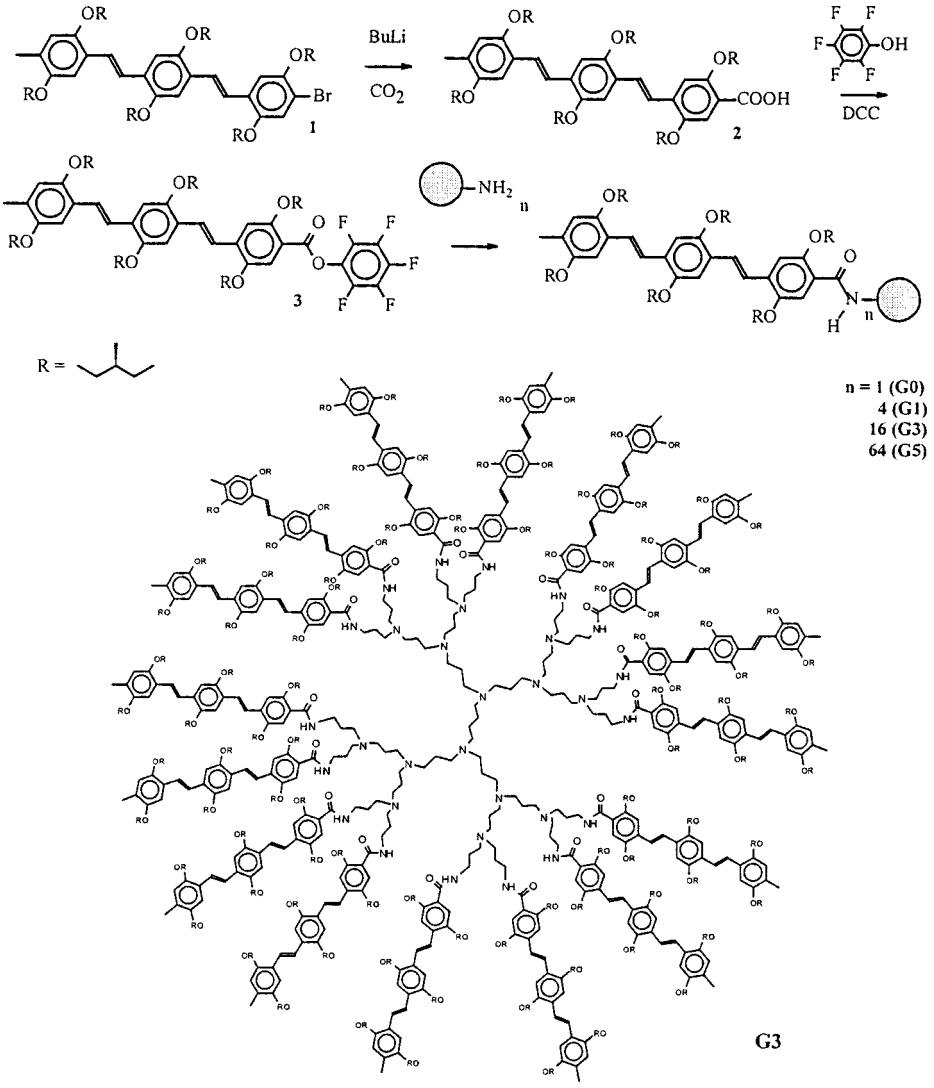
Scheme 1



due to their three-dimensional architecture, which permits spatial control of active components. As a result these materials are highly electroluminescent.[8] Moreover, such dendrimers can be applied in the construction of light-harvesting antennas[9] when using a suitable acceptor as the focal point.

In the fabrication of polychromic polymer displays there is a strong interest to adjust the emission wavelength of light emitting diodes (LED's). One of the possibilities for emission control is the addition of dye molecules with the desired emission wavelength to the semiconducting π-system.[10] A disadvantage of this approach is phase separation, which often takes place between the organic semiconductor and the polar dye molecules resulting in less efficient energy transfer. Here we describe the synthesis and characterization of poly(propylene imine) dendrimers modified with π-conjugated oligo(*p*-phenylene vinylene)s (OPV's) (Scheme 1). These macromolecules self-assemble at the air−water interface forming stable monolayers. Furthermore, these dendrimers are effective extractants of anionic dye molecules from water to organic solvents. The host−guest complexes thus obtained show energy transfer form the OPV units to the encapsulated dye molecules. These supramolecular systems improve the compatibility between organic semiconducting polymers and dyes and offer the possibility of adjusting the emission wavelength of LED's.

Results and Discussion

Synthesis and Characterization. The OPV-containing dendrimers were synthesized from tri(*p*-phenylene vinylene) derivative **1**,[11] which was converted to carboxylic acid **2** by using butyllithium and carbondioxide (Scheme 1). After reaction with pentafluorophenol in the presence of dicyclohexylcarbodiimide (DCC), the activated ester **3** was obtained. This ester was subsequently coupled to propylamine to give **G0** and to the first, third, and fifth generation poly(propylene imine) dendrimers yielding **G1**, **G3**, and **G5**, respectively. The compounds were fully characterized by IR, NMR spectroscop, and mass spectrometry. For **G5** no mass spectrum could be obtained, probably as a result of the low degree of ionization of this high molecular mass compound during the MS measurements.[3] The ^{1}H NMR spectra show the NH resonance at the same position (8.2 ppm) for all generations, implying that intramolecular H-bonding is absent. This perception is further supported by IR studies that show only free NH vibrations at 3404 cm^{-1}.[12] Functionalized

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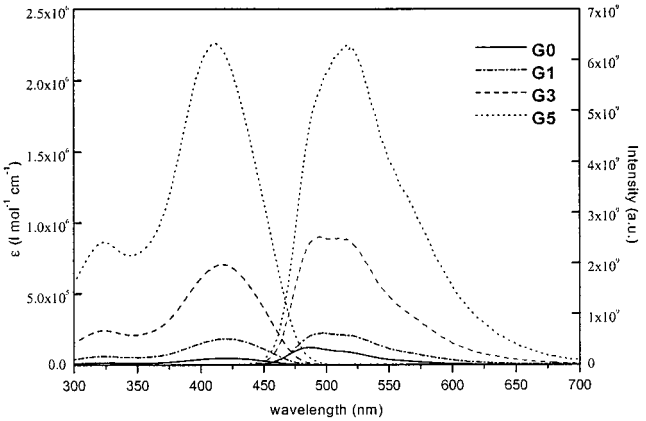

Figure 1. UV−vis (left) and fluorescence (right) spectra of **G0**, **G1**, **G3**, and **G5** in dichloromethane.

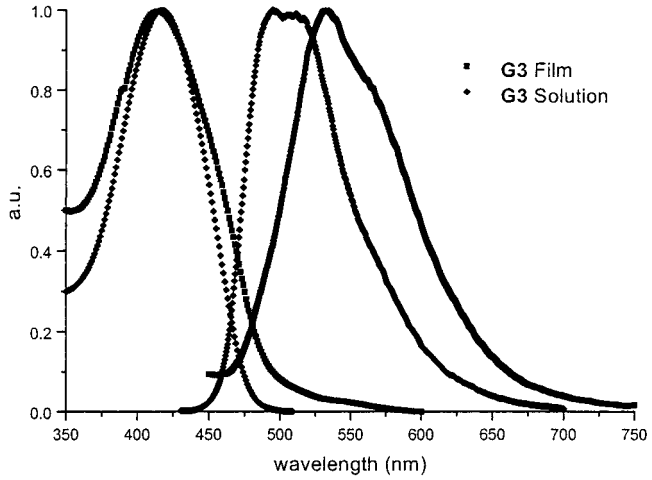

Figure 2. UV−vis (left) and fluorescence (right) spectrum of **G3** in dichloromethane and in a spin-coated film.

poly(propylene imine) dendrimers containing an amide linkage normally show intramolecular H-bonds upon going to higher generation.[13] For steric reasons, such interactions do not exist in our dendrimers, presumably due to the ortho alkoxy substituents on the benzene ring next to the amide bond.

Absorption spectra taken from the OPV dendrimers in dichloromethane show the $\pi-\pi^*$ transition of the OPV units. A small hypsochromic shift of the absorption maximum (**G0**: $\lambda_{max} = 419$ nm, **G5**: $\lambda_{max} = 412$ nm) is observed upon going to higher generations while the extinction coefficient per the tri(*p*-phenylene vinylene) unit is lowered (Figure 1). The fluorescence maxima shifts bathochromically (**G0**: $\lambda_{em,max} = 486$ nm, **G5**: $\lambda_{em,max} = 516$ nm) and the quantum yield is decreasing in the **G0**−**G5** series indicating weak interactions of π-conjugated segments in **G5**. The fact that these interactions are weak was further supported by circular dichroism (CD) measurements.[11] Despite the stereocenters present in the side chains or the OPV units, no CD effect was measured.

Amphiphilic Behavior. The self-assembly of the dendrimers was investigated at the air−water interface by the Langmuir technique. The isotherms of the OPV dendrimers are shown in Figure 3 and display a sharp increase in surface pressure upon compression, indicating the formation of stable monolayers. The stability of the monolayers was further supported by the fact

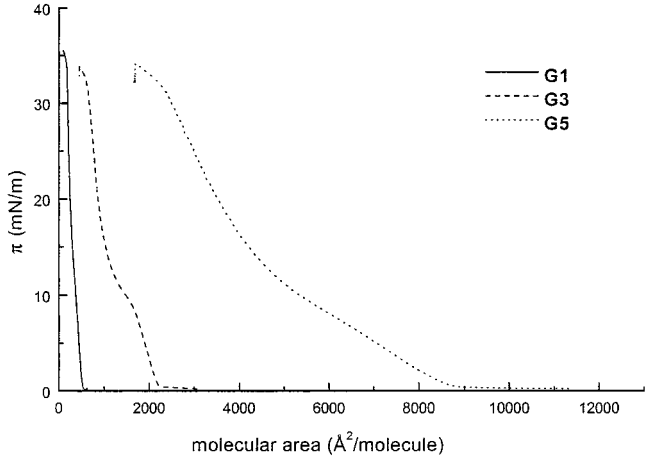

Figure 3. Langmuir layer of **G1**, **G3**, and **G5** at the air/water interface.

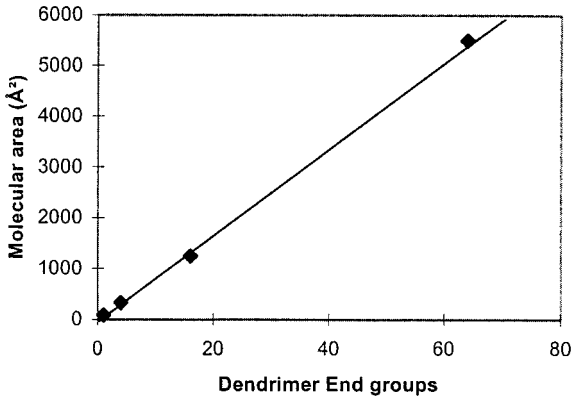

Figure 4. Molecular area of **4**, **G1**, **G3**, and **G5** as a function of the number of OPV end-groups.

that no change in the total surface area at a constant pressure for at least 1 h was observed. Brewster angle microscopy (BAM) shows that after spreading, a homogeneous film is formed, which becomes more densely packed after compression. At a pressure of $\pi = 35$ mN/m collapse of the monolayers takes place. Absorption spectra of Langmuir−Blodgett films of **G1**, **G3**, and **G5** show a maximum at 414 nm with a slightly broadened absorption line width (data not shown). No CD effect was measured in these films, indicating weak interactions between the OPV units.[11] In the case of **G0**, no LB films could be obtained because no stable monolayers were formed presumably caused by the lack of a hydrophilic poly(propylene imine) headgroup.

The area per molecule for the OPV dendrimers in the Langmuir layer was calculated by extrapolation of the steep rise in surface pressure to zero pressure.[3] The molecular areas of **G1**, **G3**, and **G5** show a linear increase with the number of OPV units attached to the different generations of dendrimers (Figure 4), a behavior similar to that found for palmitoyl functionalized poly(propylene imine) dendrimers.[3] By extrapolation, a molecular area of 86 Å^2 per OPV unit was found. Reference compound **4** (Figure 5), consisting of a polar pyridine headgroup and a hydrophobic OPV tail, was used to determine the molecular area of a single OPV unit (**G0** did not give stable monolayers, vide supra).[14] The same type of isotherm was found as in the case of the OPV dendrimers and a molecular area of 84 Å^2 was calculated, which is very close to the area found for OPV units in the dendrimers. The linear relationship between the molecular area of the dendrimers and the number of OPV

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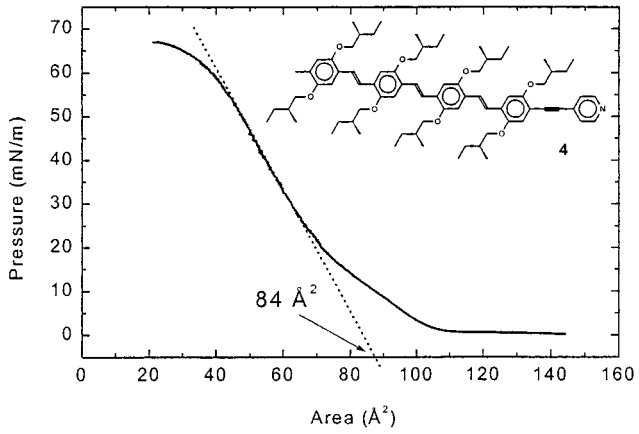

Figure 5. Langmuir layer of **4** at the air/water interface.

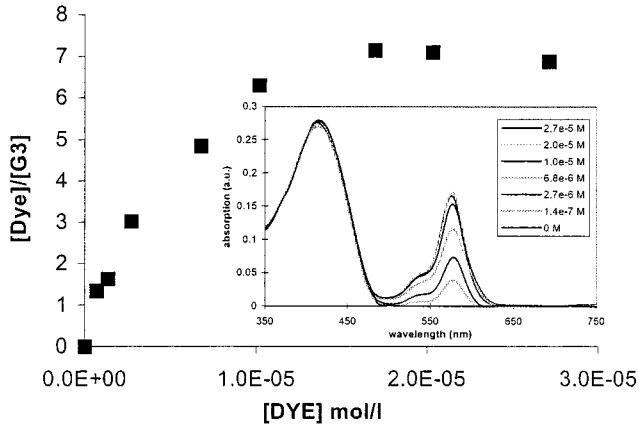

Figure 6. Sulforhodamine B to **G3** ratio of the $CHCl_3$ layer as a function of the Sulforhodamine B concentration in the aqueous layer. Inset: UV−vis spectra of the $CHCl_3$ layers showing an increase of Sulforhodamine B when the concentration of this dye in the aqueous layer is increased.

units points to a molecular orientation in which the hydrophilic dendritic poly(propylene imine) core faces the aqueous phase and all the hydrophobic OPV segments line up in a parallel fashion perpendicular to the water phase.[3] In such an arrangement, the poly(propylene imine) core is presumably flattened completely.[15]

Extraction Experiments. The OPV functionalized dendrimers are capable of extracting water-soluble anionic dyes into the organic phase with high efficiency (Figure 6).[16] When **G3** was used as extractant and Sulforhodamine B as dye a maximum of seven dyes per dendrimer could be transferred from the aqueous medium (buffer solution, pH 7) into the organic phase (Scheme 2). In the case of **G5**, this loading number was 26. The absorption maximum of the dye shows a hypsochromic shift upon encapsulation (Sulforhodamine B: $\lambda_{max} = 586$ nm (H_2O), $\lambda_{max} = 578$ nm (dendrimer−$CHCl_3$)). Complexation between host (dendrimer) and guest (dye) is mainly based on acid−base interactions between the tertiary amines and the anionic units of the guest.[5] The maximum loading values of

(15) Assuming a cylindrical shape of the OPV dendrimers at the air−water interface, a degree of flatting of the poly(propylene imine) core can be calculated from the molecular area by considering the transversal section of the dendrimer part to be a circle (see also ref 3). Radii of 10.2, 19.9, and 41.8 Å for **G1, G3**, and **G5**, respectively, were calculated indicating a high degree of flatting of the dendritic core at the air/water interface: Scherrenberg, R.; Coussens, B.; van Vliet, P.; Edourd, G.; Brackman, J.; de Brabander, E. M. M.; Mortensen, K. *Macromolecules* **1998**, *31*, 456.

(16) No dye could be extracted from the water layer when no OPV dendrimer was present in the chloroform layer.

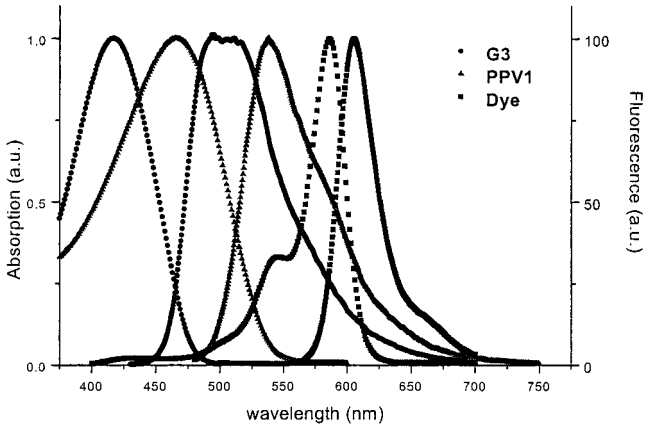

Figure 7. UV−vis and fluorescence spectra of **G3**, **PPV1** (both dichloromethane), and Sulforhodamine B (water) in solution.

dendrimer with Sulforhodamine B roughly correspond to half of the tertiary amines present in these dendrimers (**G3** contains 14 and **G5** 62 tertiary amines) and seems to indicate that both sulfonic acid units present in the dye are involved in the binding process.[17]

Energy Transfer Experiments in Solution. The host−guest systems present in the organic layer were further characterized using fluorescence spectroscopy with the aim of obtaining energy transfer between the OPV-dendrimer host and the guest. Such a transfer can be expected because of the overlap between the emission spectrum of the OPV dendrimer and the absorption spectrum of the encapsulated dye (Figure 7). When the OPV units are excited at $\lambda_{ex} = 420$ nm, the fluorescence ($\lambda_{em} = 492$ nm) is quenched and emission of the Sulforhodamine B ($\lambda_{em,max} = 593$ nm) dye is observed indicating energy transfer from the OPV trimers to the complexed dye molecules (Figure 8). The energy transfer efficiency can be calculated by determining the fluorescence quenching of the donor OPV units by comparing with the fluorescence of the OPV dendrimers without dye. It is roughly 40% for both generations of dendrimer at maximal loading. When the excitation spectrum ($\lambda_{em} = 593$ nm) and the absorption spectrum are normalized at the λ_{max} of the Sulforhodamine dye, the same efficiency value was calculated from the decrease in intensity at the λ_{max} of OPV (Figures 9 and 10). The efficiency is lower than that found in dendritic systems in which the donor and acceptor are covalently linked (varying between 60 and 100%).[9] Further examination of the fluorescence titration curves shows that the quenching curve of the OPV units is similar to that found for the extraction curve monitored by UV−vis spectroscopy, e.g. gradual change of the spectrum, which does not alter when seven dyes are bound. The fluorescence extraction curve of the dye, however, gives a steep increase in fluorescence, which levels off at a point, where on average 1−2 dyes are bound per OPV dendrimer. At that point the fluorescence increases slowly until seven dyes are encapsulated per dendrimer. The shape of the curve could indicate that due to the high local concentration of the dye in the dendrimer interior, the fluorescence of Sulforhodamine B is self-quenched. However, the absorption and fluorescence maxima of the dye do not change at different dye/dendrimer ratios. Another more likely explanation is that the first steep increase of the fluorescence points to an antenna effect. In this titration range on average one of two dye molecules is present in the host. In such a complex the peripheral OPV units can serve as antennae for harvesting photons to the encapsulated dyes. This

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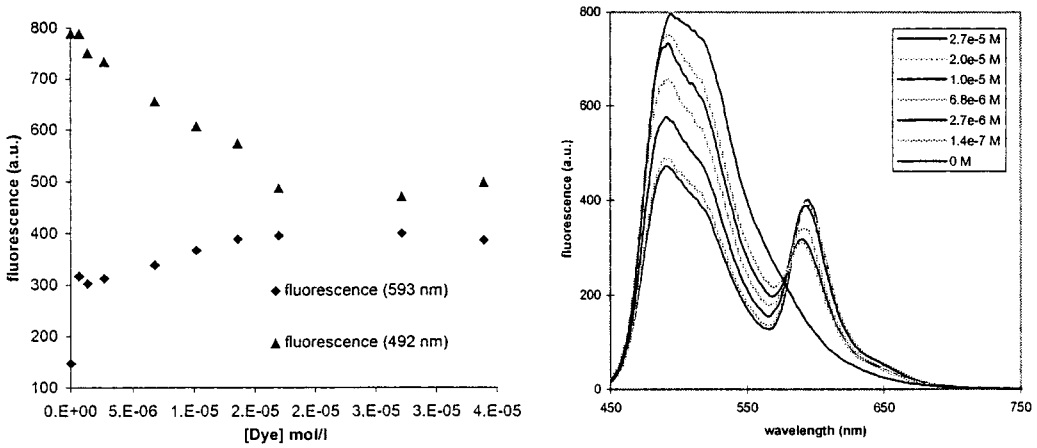
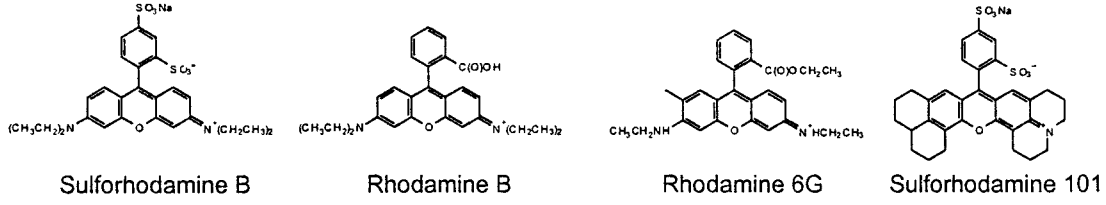


Figure 8. Ratio of the fluorescence intensity of **G3** ($\lambda_{em,max}$ = 492 nm) and Sulforhodamine B ($\lambda_{em,max}$ = 593 nm) in the chloroform layer as function of the Sulforhodamine B concentration in the water layer (left). Fluorescence spectra of the chloroform layer as a function of the Sulforhodamine B concentration in the water layer (right).

Scheme 2



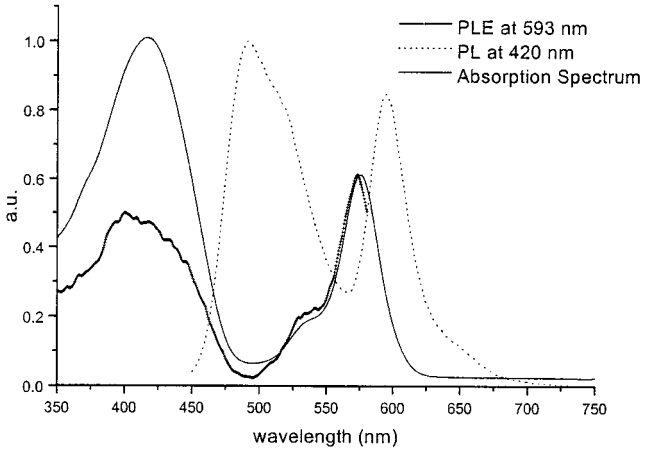


Figure 9. Absorption, excitation spectrum, and emission spectrum of a Sulforhodamine B/**G3** complex (ratio 7/1) in chloroform solution. The spectra have been normalized for ease of comparison.

behavior is supported by the same fluorescence intensity of the dye when directly excited at 578 or 420 nm. Taken into account that the energy transfer is not very efficient, this response points to an antenna function of the OPV units.

Film Properties. The dendrimers **G1**, **G3**, and **G5** could be spin-coated from a toluene solution giving good quality thin films. In the case of **G0** a nonhomogeneous very thin film was obtained. The absorption spectra of the dendrimer films (**G1**, **G3**, and **G5**) show a maximum at 414 nm with a slightly broadened absorption line width in all cases (Figure 2). The spin-coated films are still highly fluorescent with an emission maximum at 535 nm. The small blue-shifted absorption maximum and the red-shifted fluorescence maximum point to weak interactions between the OPV units. No CD effect was measured indicating that these films are highly amorphous resulting in a high fluorescence.[11] The spin-coated films have the same absorption and fluorescence maxima as was found

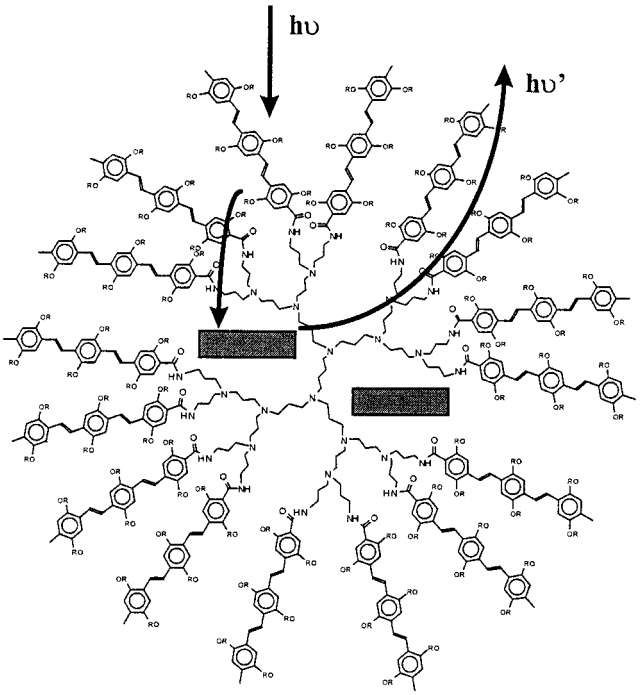


Figure 10. Schematic representation of the energy transfer process taken in the **G3**/Sulforhodamine B (black bars) complex.

for the LB films. This similarity suggests a similar local organization of OPV's, but obviously in a more symmetrical fashion in this case.

Drop casted thin films of the host/guest systems (maximal loading) show almost complete quenching of the OPV fluorescence indicating efficient energy transfer (Figure 11). By comparing the excitation spectrum (λ_{em} = 595 nm) with the absorption spectrum normalized at the λ_{max} of the Sulforhodamine B dye, an efficiency value higher than 90% was calculated. According to the Föster theory, energy transfer

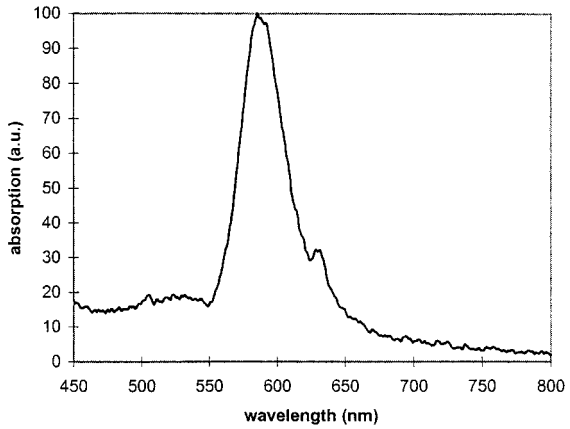


Figure 11. Fluorescence spectrum of a spin-coated film of **G3** and Sulforhodamine B (ratio = 1:7).

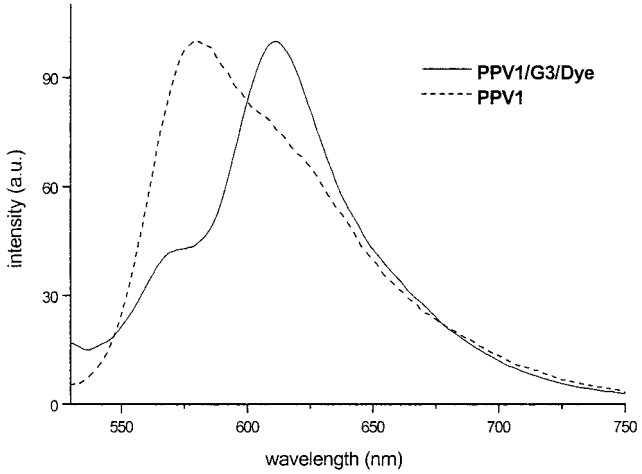


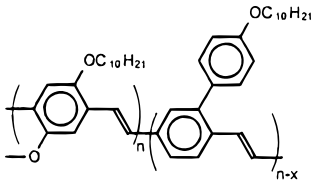
Figure 12. Fluorescence spectrum of a spin-coated film of **PPV1** and a film of **PPV1** containing **G3** and Sulforhodamine B (ratio dye: **G3** = 2:1, 10 wt %). Excitation wavelength 510 nm.

depends on the orientation of donor and acceptor. Assuming this type of energy transfer, the orientation between donor and acceptor in the film has presumably become more optimal. Another possibility is that the red-shifted fluorescence observed in spin-coated films results in a better overlap with the absorption spectrum of the dye.

The flexibility of the system was tested using other water-soluble dyes having an absorption spectrum that overlaps with the fluorescence spectrum of the OPV trimers. Thin films constructed from OPV dendrimers with Rhodamine 6G, Rhodamine 101, and Sulforhodamine 101 as acceptor show only the fluorescence of the latter ones (ranging form 560 to 640 nm), illustrating very efficient energy transfer (Scheme 2).

Eventually, the possibility of adjusting the emission wavelength of spin-coated poly(phenylene vinylene)s was investigated by the addition of the dyes. From the fluorescence spectrum of **PPV1** (Scheme 3) and dye (Figure 7) electron transfer can be expected from the conjugated polymer to the dye. Complexation of Sulforhodamine B by **G3** and subsequent addition of this complex to **PPV1** resulted after spin-coating in a homogeneous film. Fluorescence measurements show after excitation of **PPV1** at $\lambda_{ex} = 510$ nm the emission of Sulforhodamine dye at $\lambda_{em,max} = 610$ nm, indicating that energy transfer takes place (Figure 12). The efficiency is high based on the decrease in fluorescence intensity of **PPV1**. From the excitation spectrum we could not determine the efficiency of this process due to the overlap of the absorption spectrum of the polymer with **G3**. When OPV

Scheme 3



dendrimer was absent no homogeneous thin films could be obtained from a mixture of dye and **PPV1** and no energy transfer was observed. Presumably, the OPV dendrimers compatibilize ionic water-soluble dyes with **PPV1** due to the amphipilic nature.

Conclusions and Outlook

In summary, we have described the synthesis of different generations of dendrimers with peripheral OPV units. In these systems no intramolecular H-bonds exist between the amide linkages. The OPV dendrimers self-assemble at the air−water interface forming homogeneous thin films. The macromolecules extract dyes very efficiently into nonpolar solvents from aqueous phases. The ratio between dye and dendrimer can be easily varied. Thin films composed of OPV dendrimers and dyes show very efficient energy transfer. Furthermore, these supramolecular systems compatibilize ionic dyes with organic semiconducting polymers and energy transfer is observed from the organic polymer to the dyes.

The supramolecular system presented here shows high flexibility and provides a universal approach to adjusting the emission wavelength of semiconducting polymers. The emission wavelength can be tuned by using the appropriate dye from a broad set of commercially available anionic dye molecules. Preliminary experiments showed that it is possible to construct LED's from the Sulforhodamine B/**G3** system. The red color of the Sulforhodamine B dye is seen, while when only **G3** is used, the green emission of OPV units is visible. We are currently working toward the full characterization and optimization of these polymer/dye devices.

Experimental Section

General Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature on a Varian Gemini 300 or 400 MHz spectrometer. Chemical shifts are given in ppm downfield from tetramethylsilane. Abbreviations used are s = singlet, d = doublet, t = triplet, m = multiplet, and b = broad. Infrared spectra were obtained with a Perkin-Elmer spectrometer. UV−vis spectra and Fluorescence spectra were recorded on a Perkin-Elmer Lambda 40 Spectrometer and a Perkin-Elmer luminescence spectrometer LS 50 B instrument. CD spectra were recorded on a Jasco J-600 spectrometer. MALDI-TOF spectra were measured on a Perseptive DE Voyager MALDI-TOF spectrometer utilizing an α-cyano-4-hydroxycinnamic acid matrix. Monolayer experiments were performed as reported earlier.[3] Deposition experiments were carried out with a hydrophilic glass substrate, which was dipped into the subphase, and 10 layers were deposited in a Z-type depositions.[3] Spin-coated thin films were prepared by spin-casting 2 wt % toluene solutions using a Headway Research Spin-coat apparatus.

Materials. Poly(propylene imine) dendrimers were kindly provided by DSM, The Netherlands. THF (Biosolve, p.a.) was distilled over Na/benzophenone under an argon atmosphere. 1,3-Dicylcohexylcarbodiimide (DCC) (Aldrich, 99%) and pentafluorophenol (Aldrich, 99+%) were used as received. The buffer solution of pH 7 used for the extraction experiments was a phosphate buffer (Merck). Bio-Beads S-XI Beads were obtained from Bio-Rad Laboratories. **PPV1** was a gift from Dr. H. F. M. Schoo (TNO Institute of Industrial Technology, Materials Technology Division) synthesized according a literature procedure.[18]

2: To a dry THF solution (50 mL) of **1** (2.5 g, 2.8 mmol) at −78 °C under an argon atmosphere was slowly added 1.7 mL of BuLi (2.5 M in hexane). The solution changed immediately from yellow to brown. In a separate 250-mL round-bottom flask, equipped with a magnetic stirrer, an argon inlet and outlet, and a CO_2 inlet, was added 100 mL of dry THF. The solution was saturated with CO_2 during 15 min. By applying argon pressure, the dry THF solution of **1** was siphoned into the CO_2-saturated THF solution via a needle. The solution was stirred for 30 min and neutralized with acidified methanol. After evaporation of the solvent the compound was purified with flash chromatography by first using a pentane/CH_2Cl_2 (1:1, v/v) mixture as eluent to remove impurities and further with CH_2Cl_2 to obtain **2** as a yellow solid. Yield: 80%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.9−1.1 (m, 36H, CCH_3), 1.2−1.4 (m, 6H, CHH), 1.5−1.7 (m, 6H, CHH), 1.8−2.0 (m, 6H, CH), 2.2 (s, 3H, ArCH_3), 3.7−4.0 (m, 10H, OCH_3), 4.0−4.2 (m, 2H, OCH_3), 6.74 (s, 1H, ArH), 7.10 (s, 1H, ArH), 7.16 (s, 1H, ArH), 7.20 (s, 1H, ArH), 7.27 (s, 1H, ArH), 7.4−7.7 (m, 5H, ArH + ArCH═CH), 11.18 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.11, 11.31, 11.40, 16.35, 16.51, 16.65, 16.74, 26.04, 26.30, 26.32, 34.53, 34.84, 34.92, 34.96, 35.01, 35,06, 73.34 (OCH$_2$), 74.00 (OCH$_2$), 74.26 (OCH$_2$), 74.55 (OCH$_2$), 75.31 (OCH$_2$), 77.20 (OCH$_2$), 108.34, 109.64, 109.69, 110.37, 115.97, 116.13, 116.21, 121.15, 121.40, 123.68, 124.93, 125.81, 126.58, 127.81, 128.83, 133.94, 150.49, 150.87, 151.16, 151.41, 151.65, 151.82, 165.40 (C═O). MALDI-TOF MS 857.05 [M^+].

3: To a THF solution of **2** (2 g, 2.33 mmol) was added 1.1 equiv of DCC (528 mg, 2.56 mmol) at 0 °C. The reaction mixture was allowed to come to room temperature after which 468 mg (2.54 mmol) of pentafluorophenol was added. After the mixture was stirred for 14 h, THF was evaporated and the desired compound was purified with flash chromatography (pentane/CH_2Cl_2, 1:1, v/v) yielding **3** (1.66 g, 70%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.8−1.2 (m, 36H, CCH_3), 1.3−1.5 (m, 6H, CHH), 1.6−1.8 (m, 6H, CHH), 1.9−2.1 (m, 6H, CH), 2.28 (s, 3H, ArCH_3), 3.8−4.0 (m, 12H, OCH_3), 6.77 (s, 1H, ArH), 7.15 (s, 1H, ArH), 7.23 (s, 1H, ArH), 7.25 (s, 1H, ArH), 7.33 (s, 1H, ArH), 7.5−7.8 (m, 5H, ArH + ArCH═CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.26, 11.36, 11.46, 16.40, 16.50, 16.68, 16.78, 25.98, 26.25, 26.33, 26.36, 34.84, 34.95, 35.02, 35,09, 73.32 (OCH$_2$), 74.03 (OCH$_2$), 74.10 (OCH$_2$), 74.21 (OCH$_2$), 74.26 (OCH$_2$), 74.56 (OCH$_2$), 108.30, 109.71, 110.30, 114.07, 116.13, 116.73, 121.26, 121.43, 123.66, 124.94, 125.90, 126.69, 127.79, 128.81, 135.15, 149.83, 150.48, 150.87, 151.46, 151.64, 154.99, 162.25 (ArC(O)O). ^{19}F NMR ($CDCl_3$) −163.04 (sextet, 2F), −159.08 (t, 1F), −152.56 (q, 2F).

Typical Procedure for OPV Dendrimers (G3). DAB-*dendr*-$(NH_2)_{16}$ (62 mg**,** 0.04 mmol) was dissolved in dichloromethane. To this solution was added slowly a solution of **3** (650 mg**,** 0.64 mmol) in dichloromethane. After being stirred for 14 h, the reaction mixture was extracted with saturated sodium carbonate (2×). The organic layer was dried with Na_2SO_4, filtered, and dried in vacuo. The product was further purified with Bio-Beads column chromatography (CH_2Cl_2) yielding **G3** (358 mg, 59%) as a yellow solid. **G3**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.8−1.1 (m, 576H, CCH_3), 1.3−1.4 (m, 96H, CHH), 1.5−1.6 (m, 56H, NCH$_2$CH_2CH$_2$N, 4H, NCH$_2$CH_2CH_2CH$_2$), 1.6−1.7 (m, 32H, CHH), 1.7−2.0 (m, 24H, CH), 2.2 (s, 48H, ArCH_3), 2.60 (t, br, 84H, NCH_2-CH$_2$CH_2N, NCH_2CH$_2$CH$_2$CH_2N, C(O)NHCH$_2$CH$_2$CH_2), 3.47 (s, br, 32H, C(O)NHCH_2), 3.7−4.0 (m, 192H, OCH_2), 6.70 (s, 16H, ArH), 7.07 (s, 16H, ArH), 7.1−7.2 (s, 48H, ArH), 7.4−7.5 (m, 64H, ArCH═CH), 7.71 (s, 16H, ArH), 8.17 (t, br, 16H, NH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.40, 11.52, 11.61, 14.26, 16.54, 16.80, 16.83, 16.86, 16.90, 22.77, 25.70, 26.33, 26.37, 26.41, 26.42, 27.19, 31.68, 34.80, 34.99, 35.02, 35.04, 35.09, 35.14, 38.29, 73.27, 73.88, 73.94, 74.12, 74.56, 108.09, 109.29, 109.49, 109.95, 115.38, 116.10, 120.51, 121.38, 121.63, 122.96, 124.62, 124.93, 126.27, 127.39, 127.88, 130.81, 150.20, 150.42, 150.63, 150.69, 150.99, 151.40, 164.87. IR (KBr) ν (cm^{-1}) 3404.0 (N−H stretch), 2959.0 (C−H sat), 2929.6 (C−H sat), 2873.2 (C−H sat), 1636.1 (C═O). MALDI-TOF MS 15116.5 [M^+], calcd 15111. UV/vis ($CHCl_3$): λ_{max} (ϵ) = 324 (241 000), 417 nm (704 000).

G0: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.8−1.2 (m, 39H, CH_3), 1.3−1.5 (m, 6H, CHH), 1.6−1.7 (m, 8H, CHH, NCH$_2$CH_2), 1.9−2.0 (m, 6H, CH), 2.26 (s, 3H, ArCH_3), 3.46 (q, 2H, CH_2N), 3.8−4.1 (m, 12H, OCH_3), 6.75 (s, 1H, ArH), 7.12 (s, 1H, ArH), 7.19 (s, 1H, ArH), 7.21 (s, 1H, ArH), 7.23 (s, 1H, ArH), 7.4−7.6 (m, 4H, ArCH═CH), 7.79 (s, 1H, ArH), 8.27 (t, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.38, 11.50, 11.55, 11.60, 11.76, 16.54, 16.90, 16.94, 22.89, 26.33, 26.42, 26.45, 29.78, 34.98, 35.02, 35,09, 35.16, 41.73, 73.32, 73.92, 74.04, 74.20, 74.24, 74.59, 108.19, 109.36, 109.64, 110.11, 115.41, 116.13, 120.20, 121.39, 121.63, 123.22, 124.88, 124.92, 126.20, 127.55, 128.11, 131.09, 150.23, 150.51, 150.69, 151.02, 151.09, 151.44, 165.22; IR (KBr) ν (cm^{-1}) = 3404.0 (N−H stretch), 3349.1 (N−H stretch), 2959.0 (C−H sat), 2929.6 (C−H sat), 2873.2 (C−H sat), 1636.1 (C═O). MALDI-TOF MS 897.50 [M^+], calcd 897.65. UV/vis ($CHCl_3$): λ_{max} (ϵ) = 324 (15 600), 419 nm (46 000).

G1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.8−1.2 (m, 144H, CCH_3), 1.2−1.4 (m, 24H, CHH), 1.46 (m, 4H, NCH$_2$CH_2CH_2CH$_2$), 1.6−1.7 (m, 32H, CHH), 1.79 (m, 8H, C(O)NHCH$_2$CH_2), 1.8−2.0 (m, 24H, CH), 2.2 (s, 12H, ArCH_3), 2.47 (s, br, 4H, NCH_2CH$_2$CH$_2$CH_2), 2.56 (t, 8H, C(O)NHCH$_2$CH$_2$CH_2), 3.51 (q, 8H, C(O)NHCH_2), 3.7−4.0 (m, 48H, OCH_2), 6.74 (s, 1H, ArH), 7.11 (s, 4H, ArH), 7.18 (s, 4H, ArH), 7.19 (s, 4H, ArH), 7.22 (s, 4H, ArH), 7.5−7.6 (m, 16H, ArCH═CH), 7.78 (s, 4H, ArH), 8.20 (t, 4H, NH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.46, 11.50, 11.55, 11.60, 16.54, 16.81, 16.86, 16.91, 16.95, 16.99, 25.19, 26.33, 26.41, 26.43, 27.66, 29.44, 29.77, 34.91, 34.98, 35.00, 35.07, 35,09, 35.15, 38.38, 51.83, 54.16, 73.29, 73.92, 74.01, 74.16, 74.20, 74.57, 108.15, 109.42, 109.59, 110.07, 115.41, 116.10, 120.56, 121.38, 121.66, 123.13, 123.76, 124.88, 126.23, 127.49, 128.02, 130.88, 150.21, 150.49, 150.65, 150.98, 151.42, 164.86. IR (KBr) ν (cm^{-1}) = 3404.0 (N−H stretch), 2959.0 (C−H sat), 2921.3 (C−H sat), 2874.2 (C−H sat), 1654.8 (C═O). MALDI-TOF MS 3696.88 [M^+], calcd 3697.41. UV/vis ($CHCl_3$) λ_{max} (ϵ) = 324 (61 000), 419 nm (182 000).

G5: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.8−1.1 (m, 2304H, CCH_3), 1.1−1.3 (m, 384H, CHH), 1.4−1.6 (m, 4H, NCH$_2$CH_2CH_2CH$_2$N, 120H, NCH$_2$CH_2CH$_2$N, 384H, CHH), 1.7−1.9 (m, 384H, CH), 2.25 (s, br, 192H, ArCH_3), 2.60 (s, br, 128H, C(O)NHCH$_2$CH$_2$CH_2, 4H, NCH_2-CH$_2$CH$_2$CH_2N, 240H, NCH_2CH$_2$CH_2N), 3.4−4.0 (m, 768H, OCH_2, 128H, C(O)NHCH_2), 6.64 (s, br, 64H, ArH), 7.07 (s, 64H, ArH), 7.1−7.03 (s, 192H, ArH), 7.4 (s, br, 256H, ArCH═CH), 7.62 (s, br, 64H, ArH), 8.10 (s, br, 64H, NH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.40, 11.48, 11.58, 14.19, 16.49, 16.73, 16.83, 22.79, 23.04, 24.70, 26.29, 26.36, 27.68, 29.78, 34.64, 34.98, 35,04, 35.11, 38.31, 73.15, 73.73, 73.90, 74.45, 107.81, 108.87, 109.17, 109.48, 115.38, 116.01, 120.78, 121.27, 122.52, 123.97, 124.98, 126.30, 127.09, 127.51, 130.34, 150.10, 150.22, 150.51, 150.82, 150.90, 151.31, 164.56. IR (KBr) ν (cm^{-1}) = 3404.0 (N−H stretch), 2959.7 (C−H sat), 2929.6 (C−H sat), 2873.2 (C−H sat), 1653.9 (C═O). UV/vis ($CHCl_3$): λ_{max} (ϵ) = 324 (862 000), 412 nm (2 256 000).

Extraction Experiments. In a test tube 5 mL of a chloroform solution of **G3** or **G5** was added. Additionally 5 mL of an aqueous solution (buffer, pH 7) of dye was added. Concentrations were in the order of 10^{-6} M. After the mixture was vortexed for 2 min, the two phases were separated using a centrifuge and both the aqueous and organic phase were sampled by UV−vis spectroscopy to determine the extraction yield.[5] In all cases a decrease in absorption of the aqueous layer simultaneously gives an increase in absorption of the dye in the organic layer.

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