Polarizing Energy Transfer in Photoluminescent Conjugated Polymers with Covalently Attached Sensitizers

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ABSTRACT: A new class of poly(*p*-phenyleneethynylene) (PPE) polymers, COU-OPPE and ANT-OPPE, have been prepared, in which coumarin- and anthracene-based sensitizer molecules are covalently linked to the conjugated polymer backbone via a flexible spacer. In dilute solutions of these polymers, efficient resonance energy transfer is observed from the sensitizer moieties to the PPE backbone, resulting in enhanced luminescence of the PPE macromolecules. Also, when incorporated as guests in oriented polyethylene films, the novel polymers, COU-OPPE and ANT-OPPE, show efficient energy transfer from the pendent sensitizer to the PPE backbone. Especially in the case of ANT-OPPE, we found that the PPE backbone is efficiently oriented while the anthracene moiety remains essentially isotropic, which results in a high degree of *polarizing* energy transfer for this system.

Introduction

Recent efforts to increase the efficiency of liquid crystal displays (LCD's) have, among others,[1] focused on the incorporation of photoluminescent (PL) polarizers in a new family of PL LCD's.[2] It has been shown that PL polarizers can generate bright colors with a high degree of polarization of the emitted light, by using uniaxially oriented, highly photoluminescent polymers.[3] To overcome the problem that such PL polarizers not only emit light anisotropically but also absorb incident light in a highly polarized fashion, an isotropically absorbing dye was introduced into the PL polarizer to act as a light-harvesting sensitizer.[4] The latter absorbs the light isotropically and subsequently transfers the energy to the oriented PL polymer, which then emits polarized light. In this *polarizing* energy transfer, the isotropic dye acts as a donor and the PL polymer as an acceptor and emitter. As a result of the high efficiency of the polarizing energy transfer, the performance of these new polarizers has been dramatically improved compared to the reference, unsensitized PL polarizers. In our previous studies, a poly(2,5-dialkoxy-*p*-phenyleneethynylene) derivative (EHO-OPPE) (Figure 1) was used as the PL polymer, and a variety of form-isotropic low-molecular weight dyes such as 7-(diethylamino)-4-methylcoumarin were employed as the sensitizer.[4] These chromophores were dispersed in an ultrahigh molecular weight polyethylene (UHMW PE) matrix by a gel-processing route, and orientation of the PPE molecules in films of these blends was introduced by tensile deformation at elevated temperatures. For a generalization of this approach, however, problems resulting from the required molecular proximity of the donor (the isotropic sensitizer) and the acceptor (the PL polymer) and difficulties related to the delicate phase behavior in multicomponent systems are to be expected.

To circumvent the above-described disadvantages of such blends, we now explore to chemically attach the sensitizer moieties to the conjugated polymer backbone (Scheme 1). Recently, a similar concept has been advanced for light-emitting diodes (LED's) based on poly(phenylenevinylene)s (PPV's). In this latter case, multifunctional PPV polymers with electron-transporting oxadiazole side chains attached to the conjugated polymer backbone have been successfully applied in single-layer LED's, which showed an improved performance.[5] Furthermore, a number of polymers such as polystyrene,[6] polynorbornene,[7,8] and others[9,10] have been functionalized with pendent luminescent compounds such as oxadiazole,[5,6,9] diphenylanthracene,[8,10] and coumarin[7] to enhance the processability of the luminescent labels and compatibility between organic molecules and polymeric matrices. Although PPE's have been widely studied for applications in chemosensors,[11] LED's,[12,13] and LCD's,[2] to the best of our knowledge, no attempts have been reported to covalently link such functional groups to the PPE backbone.[14]

Here, we present results of our efforts toward a versatile synthesis of PPE's with sensitizers covalently attached to the conjugated polymer backbone, with the ultimate goal to further improve the polarizing energy transfer in uniaxially oriented films of these materials. To examine the broader applicability of our approach, different PPE polymers, ANT-OPPE and COU−OPPE,

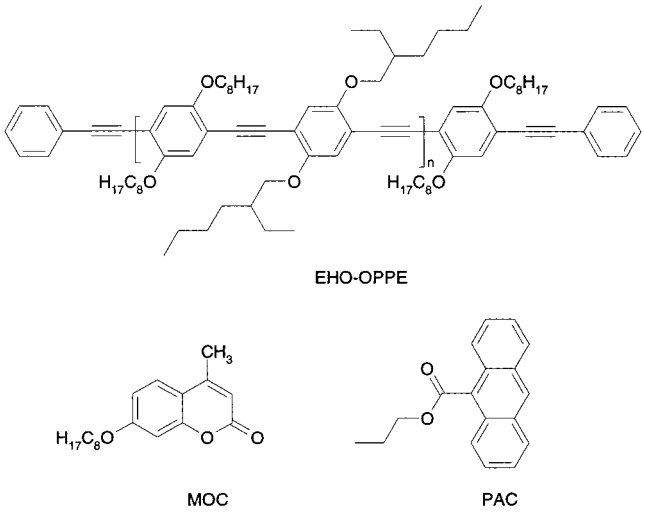

Figure 1. Model compounds EHO-OPPE (emitter) and MOC and PAC (sensitizers).

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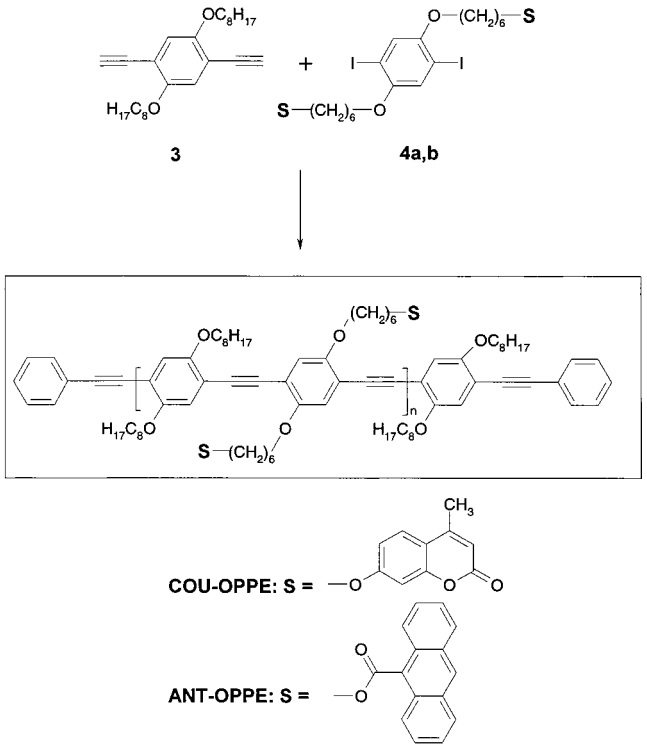
Scheme 1. Heck Synthesis of COU-OPPE and ANT-OPPE: $Pd(PPh_3)_4$/CuI, Iodobenzene, Toluene/ Diisopropylamine, Yield 44−70%



with anthracene and coumarin moieties covalently attached via a flexible spacer were prepared (Scheme 1). The polymers were processed into blend films with UHMW PE as the matrix material, according to procedures previously described.[2,3] For the purpose of comparison, model compounds 4-methyl-7-octyloxycoumarin (MOC) and propyl 9-anthracenecarboxylate (PAC) (Figure 1) were also synthesized and processed together with unsubstituted EHO-OPPE and UHMW PE in a similar fashion. The influence of attaching rather large sensitizers on the orientation behavior of the PPE backbone was investigated, and the results are discussed in terms of the thermal behavior of the novel PPE polymers.

Results and Discussion

Synthesis and Characterization of COU-OPPE and ANT-OPPE. PPE's are typically synthesized by a cross-coupling polymerization under Heck conditions of a diiodoaryl monomer with a diethynyl monomer (Scheme 1).[15] To allow for the coupling of a variety of sensitizers to the PPE backbone, we developed a synthesis strategy based on the use of the intermediates 1,4-diiodo-2,5-dihydroxybenzene (**1**)[11a] and 1,4-diiodo-2,5-di(6-hydroxyhexyl-1-oxy)-benzene (**2**) (Scheme 2). The synthesis of compound **1** is well established, while compound **2** proved to be easily accessible via the alkylation of **1** with 6-bromohexanol in K_2CO_3/DMF. Thus, monomers **4a** and **4b** were synthesized by the coupling of **2** with 7-hydroxy-4-methylcoumarin and 9-anthracenecarboxylic acid, respectively. The selection of these sensitizers was based on their favorable spectral characteristics, their form isotropy, and the straightforward methods to couple these moieties with primary aliphatic alcohols.

The resulting derivatized diiodoaryl monomers **4a** and **4b** were polymerized with 1,4-diethynyl-2,5-bis(octyloxy)benzene (**3**) according to well-established procedures,[16] which afforded the new polymers COU-OPPE and ANT-OPPE in reasonable yields (44−70%). Compound **3** was used as the diethynyl monomer in all cases due to its easy (synthetic) accessibility.[16] To control the molecular weight of the polymers, the ratio of the two bifunctional monomers was carefully adjusted. In addition, iodobenzene was added to ensure that the polymers have well-defined, nonreactive end groups.[16] While polymers ANT1-OPPE and ANT2-OPPE remained soluble during polymerization, COU-OPPE precipitated. All polymers were purified by precipitation from $CHCl_3$/MeOH mixtures and were obtained as yellow, fluffy powders.

Reference model compounds MOC,[17] PAC,[18] and EHO-OPPE[16] (Figure 1) were synthesized according to previously described procedures. Both model compounds, MOC and PAC, were selected because of their favorable physicochemical compatibility with the PPE emitter. In fact, MOC and PAC were found to be good solvents for EHO-OPPE at elevated temperatures. In addition, these model compounds MOC and PAC have relatively low melting points which ensures a beneficial[4b] high mobility during deformation of UHMW PE based blends.

All polymers were fully characterized by ^{1}H NMR spectroscopy, elemental analysis, UV−vis, and steady-state photoluminescence spectroscopy. Number-average molecular weights were determined by end-group analysis of the ^{1}H NMR spectra and by gel-permeation chromatography (GPC) measurements in $CHCl_3$, relative to polystyrene standards; the results are summarized in Table 1. For comparison, the data of EHO-OPPE are also included.

Figure 2 shows the ^{1}H NMR spectrum of COU-OPPE in CD_2Cl_2. All aromatic peaks of the polymer backbone and the coumarin side group are relatively sharp, indicating that the molecular weight of COU-OPPE is not very high. Furthermore, the signals of the protons of the phenyl end groups can be clearly distinguished around 7.5 and 7.3 ppm. Since COU-OPPE is quantitatively end-capped with phenyl groups, the number-average degree of polymerization, $\bar{x}_n$,[19] can be determined by the integration of the phenyl end group and pendent coumarin side group signals. This resulted for COU-OPPE in a number-average molecular weight, $\bar{M}_n$, of 6500 g/mol and an $\bar{x}_n$ of 13. The latter is in good agreement with the calculated value of 14.[20] Polymers ANT1-OPPE and ANT2-OPPE exhibit similar spectra, in which the chemical shifts of the end groups are sufficiently separated to enable an estimation of $\bar{x}_n$. In this case, the values for $\bar{M}_n$ were 6600 and 14 300 g/mol for ANT1-OPPE and ANT2-OPPE, respectively. The polydispersity indices of the polymers were estimated using GPC measurements, relative to polystyrene standards. Since PPE's comprise a rigid-rod polymer backbone and polystyrene calibration is well-known to lead to significant errors in the determination of the absolute molecular weight in case of rigid-rod polymers,[21] the molecular weights of ANT-OPPE and COU-OPPE resulting from GPC measurements are expected to deviate from those obtained by ^{1}H NMR end-group analysis. Indeed, as demonstrated in Table 1, the molecular weights measured by GPC demonstrate a consistent and systematic overestimation when compared to the molecular weights obtained by ^{1}H NMR end-group analysis. The polydispersity indices were between 2.3 and 2.9, i.e., in the standard range for polycondensations.

Scheme 2. Synthesis of Monomers 4a and 4b: (a) 6-Bromohexanol, K_2CO_3, DMF, 3 days, 39%; (b) 7-Hydroxy-4-methylcoumarin, PPh_3, DEAD, THF, 18 h, 46%; (c) 9-Anthracenecarboxylic Acid, Trifluoroacetic Anhydride, CH_2Cl_2, 18 h, 70% (DEAD = Diethylazodicarboxylate)

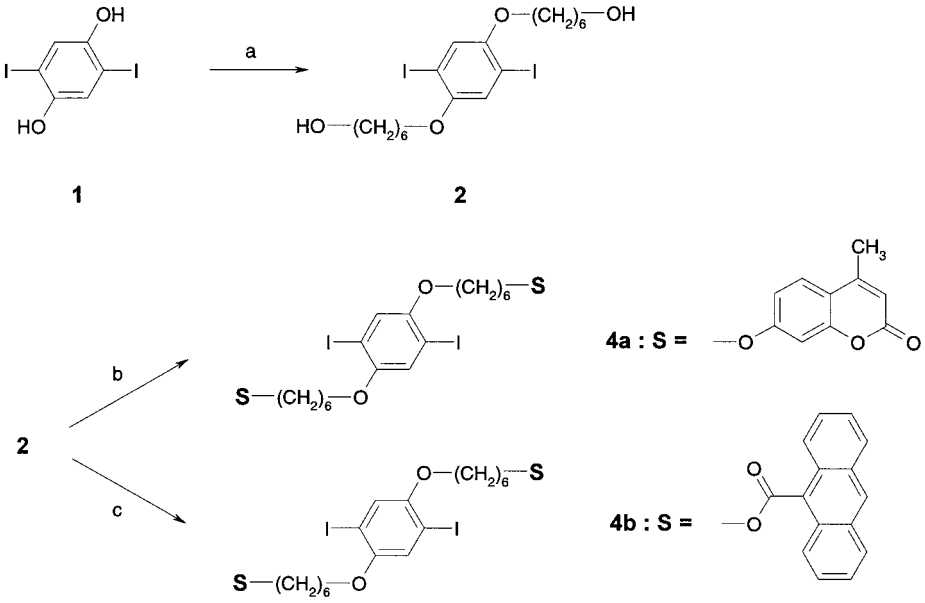


Table 1. Molecular Weights of Sensitizer-Derivatized PPE's

polymer	$\bar{x}_n$[a]	$\bar{M}_n$ [g/mol][a]	$\bar{M}_n$ [g/mol][b]	$\bar{M}_w/\bar{M}_n$[b]
COU-OPPE	13	6.5×10^3	10.5×10^3	2.8
ANT1-OPPE	12	6.6×10^3	10.0×10^3	2.3
ANT2-OPPE	26	14.3×10^3	19.3×10^3	2.9
EHO-OPPE	20	7.1×10^3	13.3×10^3	2.2

[a] Number-average degree of polymerization ($\bar{x}_n$) and number-average molecular weight ($\bar{M}_n$), determined by end group analysis of the ^{1}H NMR spectra. [b] Number-average molecular weight ($\bar{M}_n$) and polydispersity ($\bar{M}_w/\bar{M}_n$) determined by gel-permeation chromatography (GPC), relative to polystyrene standards.

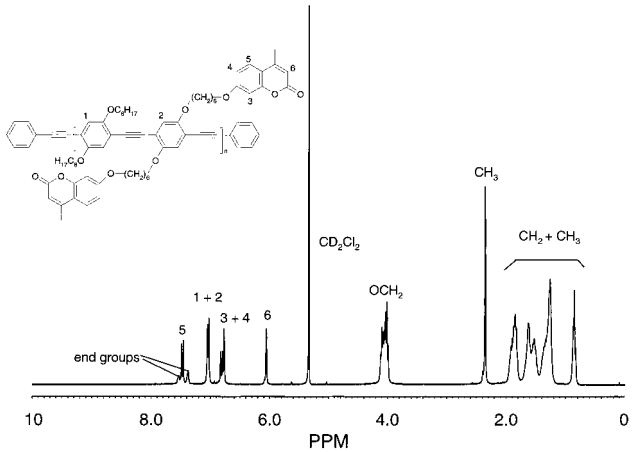


Figure 2. ^{1}H NMR spectrum (500 MHz) of COU-OPPE in CD_2Cl_2.

The thermal behavior of the new polymers, COU-OPPE and ANT-OPPE, was investigated using differential scanning calorimetry (DSC) at heating and cooling rates of 10 K/min and polarization microscopy. The latter technique, with crossed polarizers, showed that COU-OPPE displayed some crystallinity at room temperature. The crystallinity was found to slowly increase upon heating, and the polymer remained in a "nonmobile" phase up to 150 °C, where the polymer transformed into a fluid, isotropic phase and simultaneously decomposed. DSC scans (first heating run) confirmed that a pronounced, irreversible exothermic transition (most likely cross-linking of the polymer)[22] was present at 157 °C. A second, exothermic transition at around 45 °C in the first DSC heating scan could not be distinguished unequivocally by polarization microscopy but might be attributed to the glass transition of the amorphous fraction. By contrast, both polymers ANT1-OPPE and ANT2-OPPE formed a highly mobile and birefringent phase starting from around 50 °C. Above 130 °C, the polymers became isotropic and started to decompose. DSC measurements confirmed the onset of decomposition around 130 °C for both ANT-OPPE derivatives and a transition around 45 °C, which we attribute to a glass transition. Previously, the observation of birefringence after shearing the melt in alkyl- and alkoxy-substituted PPE's has been assigned to an unidentified thermotropic liquid crystalline phase.[23] In addition, we observed that also EHO-OPPE—which has a T_g of 90 °C[16,22]—shows shear birefringence around the isotropization temperature (~155 °C). These observations and the fact that anthracene side groups may act as a solvent to solubilize the rigid PPE backbone point to the presence of a liquid crystalline phase between the glass transition temperature and the decomposition temperature in ANT-OPPE. Unfortunately, characteristic textures to enable identification of the mesophase have not been observed.

Energy Transfer in COU-OPPE and ANT-OPPE in Solution. UV and PL spectra were taken of diluted solutions of COU-OPPE and ANT-OPPE in $CHCl_3$. In all cases, the optical path length was 1 cm, and the solutions had an optical density of ~0.1. The molar extinction coefficients ϵ and the maxima of absorption ($\lambda_{max,A}$) and emission ($\lambda_{max,E}$) are summarized in Table 2, together with the respective data for EHO-OPPE, which serves as a reference. To assess the influence of the covalently attached sensitizers on the PL properties of the PPE, PL quantum efficiencies (Φ) were determined. The PL quantum efficiency was measured in $CHCl_3$ with EHO-OPPE as a reference—the absolute quantum yield of which was earlier reported to be 0.85[16]—and by directly exciting the PPE backbone at 440

Table 2. Photophysical Properties of Sensitizer-Derivatized PPE's and Model Compounds in Solution ($CHCl_3$)

compound	$\lambda_{max,A}$[a] [nm]	ϵ[b] [L mol^{-1} cm^{-1}]	$\lambda_{max,E}$[a] [nm]	Φ_{ET}[c]	Φ[d]
COU-OPPE	438	4.7×10^4	474	0.80	0.81
ANT1-OPPE	438	4.7×10^4	474	0.88	0.78
ANT2-OPPE	442	4.7×10^4	475	0.74	0.72
EHO-OPPE	448	5.2×10^4	477	n.a.[f]	0.85[e]
MOC	323	1.6×10^4	373	n.a.[f]	
PAC	364	0.7×10^4	469	n.a.[f]	

[a] Maxima of absorption ($\lambda_{max,A}$) and emission ($\lambda_{max,E}$). [b] Per mole of the polymer repeat unit. [c] Energy transfer efficiency, calculated according to ref 24. [d] Absolute quantum efficiency under excitation at 440 nm and measured relative to EHO-OPPE. [e] Absolute quantum efficiency as previously published.[16] [f] n.a. = not applicable.

nm, i.e., at a wavelength at which neither of the sensitizers shows any absorption.

Small changes in $\lambda_{max,A}$ of the polymers COU-OPPE and ANT-OPPE can be discerned: 438 nm for COU-OPPE and ANT1-OPPE and 442 nm for ANT2-OPPE. As ^{1}H NMR and GPC results indicate that the molecular weight of polymers COU-OPPE and ANT1-OPPE is rather low, we suspect that their effective conjugation lengths may not yet have been reached. This is fully consistent with the results of Le Moigne et al. where the effective conjugation length in solution of poly(2,5-didodecyloxy-*p*-phenyleneethynylene) is only reached at a degree of polymerization $\bar{x}_n$ of approximately 27.[24] Indeed, a 4 nm difference is found in $\lambda_{max,A}$ when ANT1-OPPE ($\bar{x}_n = 12$) is compared to is higher molecular weight analogue ANT2-OPPE ($\bar{x}_n = 26$). Despite the similar $\bar{M}_n$ of ANT2-OPPE and EHO-OPPE, $\lambda_{max,A}$ is still notably different: 442 vs 448 nm for ANT2-OPPE and EHO-OPPE, respectively. Most likely, the voluminous anthracene side groups influence the planarity of the PPE backbone and, as a result, lower $\lambda_{max,A}$. On the other hand, ϵ and $\lambda_{max,E}$ are comparable for the polymers COU-OPPE and ANT-OPPE within error limits.

The new polymers, COU-OPPE and ANT-OPPE, were found to be highly emissive as evidenced by their high PL quantum efficiencies, Φ, of 0.72−0.81. This indicates that the PL properties of the PPE backbone are hardly affected by the pendent sensitizers. The origin of the somewhat lower PL quantum efficiency found for ANT2-OPPE ($\Phi = 0.72$) is not completely understood but might be attributed to small impurities or defects (e.g., iodine end groups) present in this polymer which are evidenced by a noticeable deviation of the carbon content in elemental analysis.

The occurrence of energy transfer in $CHCl_3$ solution from the sensitizer (donor) to the PPE backbone (acceptor) can be demonstrated either by establishing whether the emission of the sensitizer is absent in the emission spectrum of the solution when excited at the absorption maximum of the sensitizer or, alternatively, by conducting excitation scans at a wavelength where the sensitizer does not emit.[25] In the latter, a maximum should be found at the absorption maximum of the sensitizer if energy transfer does occur. As a reference, solutions of EHO-OPPE also containing the model compounds MOC and PAC were prepared. The concentration and the ratio of the sensitizer and EHO-OPPE in the reference solutions were adjusted to match the ones of the copolymer solutions. The absorption and emissions scans of COU-OPPE, ANT1-OPPE, EHO-OPPE, and respective mixtures of EHO-OPPE and the model compounds MOC and PAC are shown in Figure 3a,b. The spectra of ANT2-OPPE are omitted since they are essentially identical to those of ANT1-OPPE. The relevant spectroscopic data are summarized in Table 2.

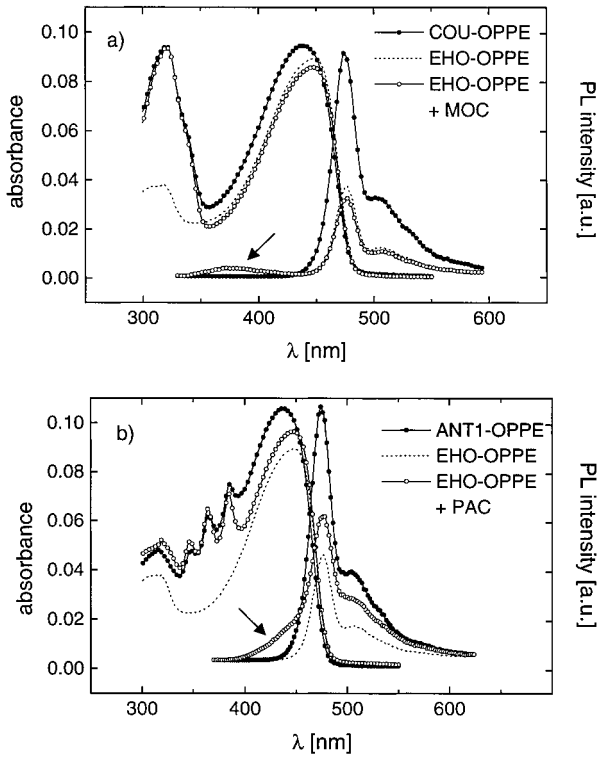


Figure 3. Absorption and emission spectra in $CHCl_3$ of (a) COU-OPPE and reference solutions and (b) ANT1-OPPE and reference solutions. In all cases, the optical path length was 1 cm and the solutions had an optical density of ∼0.1.

The absorption spectra in Figure 3a,b suggest that there is no influence of the sensitizer on the electronic properties of the PPE backbone: the absorption spectra of COU-OPPE and ANT1-OPPE are superpositions of the spectra of model compounds MOC or PAC with EHO-OPPE. Furthermore, in the emission scans of COU-OPPE and ANT-OPPE ($\lambda_{ex} = 320$ nm for COU-OPPE and $\lambda_{ex} = 365$ nm for ANT-OPPE) no emission of the sensitizer can be identified. By contrast, emission scans of the reference solutions of EHO-OPPE with MOC or PAC clearly show residual sensitizer emission as indicated in Figure 3a,b. Excitation scans under detection at 580 nm (i.e., at a wavelength were the emission is exclusively related to the PPE backbone) reveal a prominent peak at ∼320 nm (the absorption maximum of the sensitizer) in case of COU-OPPE while in case of the mixture of MOC and EHO-OPPE no significant peak at ∼320 nm is observed (Figure 4). Since the anthracene unit emits at 580 nm as well, excitation scans with detection at 580 nm are deemed not to be reliable for confirming the presence of energy transfer in this case.

Thus, applying our above criteria, it is evident that energy transfer occurs from the sensitizer to the PPE backbone in COU-OPPE and ANT-OPPE. Since the solutions of EHO-OPPE mixed with the sensitizers MOC and PAC do show a residual emission of the sensitizer, in these systems the efficiency of the energy transfer from the sensitizer to the PPE backbone evidently is limited. For COU-OPPE the presence of energy transfer is further substantiated by the presence of a clear maximum at 320 nm in the excitation scan.

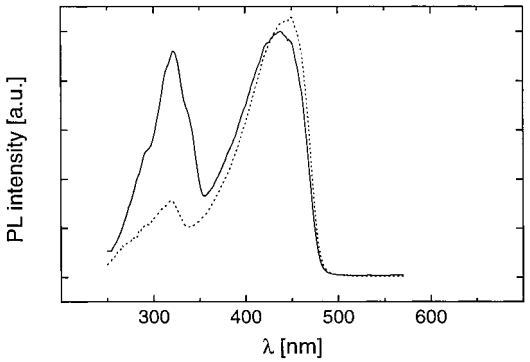


Figure 4. Excitation spectra (normalized) recorded under detection at 580 nm of COU-OPPE (solid line) and MOC/EHO-OPPE (dotted line) in $CHCl_3$.

To quantify the results presented above, the efficiency of the energy transfer, Φ_{ET}, in COU-OPPE and ANT-OPPE was calculated using well-established methodologies;[26] the results are given in Table 2. The values were found to be around 80% for all three polymers, indicating an efficient energy transfer process in solution. The lower energy transfer efficiency of 74% in case of ANT2-OPPE compared to its low molecular weight analogue ANT1-OPPE (Φ_{ET} = 88%) is in accordance with the slightly lower PL quantum efficiencies of the former polymer (see above).

Orientation Behavior of COU−OPPE and ANT-OPPE in UHMW PE. Binary blends based on a UHMW PE matrix and 2% w/w of the new polymers, COU-OPPE and ANT-OPPE, were prepared by solution casting from *p*-xylene according to previously described procedures.[3] For comparison, ternary reference blends of MOC/EHO-OPPE/UHMW PE and PAC/EHO-OPPE/UHMW PE and binary reference blends of MOC/UHMW PE and PAC/UHMW PE were prepared as well. All blends were uniaxially oriented by tensile deformation at 120 °C. The films were characterized by draw ratios between 70 and 80 and a final thickness of ∼2 μm. The photophysical characteristics of all films based on the ternary and binary blends were investigated with polarized UV absorption and steady-state PL spectroscopy. UV spectra were taken with incident light polarized parallel (p) and perpendicular (s) to the orientation direction. From these data, the dichroic ratio in absorption, DR_A, was calculated. DR_A was determined at a fixed wavelength since the dichroic behavior is wavelength-dependent. PL spectra were obtained under isotropic excitation at 440 nm and p- and s-polarized detection; the dichroic ratio in emission, DR_E, was obtained by integration of the respective emission spectra because the integrals are directly related to the energy of the relevant electronic transitions (see Experimental Procedures for details). The DR_E (given in Table 3 for excitation at 440 nm) was found to be independent of the excitation wavelength as evidenced by the similar dichroic ratios obtained for excitation at 440 and 320 nm (for coumarin-based blends) or 365 nm (for anthracene-based blends). The data are summarized in Table 3.

Both sensitizers, MOC and PAC, remained essentially unoriented after tensile deformation, as evidenced by the low dichroic ratios in both absorption and emission. The anthracene derivative PAC (DR_A = 1.1, DR_E = 1.1) was more isotropic than the coumarin derivative MOC (DR_A = 1.8, DR_E = 1.5). Also in the ternary reference blends comprising EHO-OPPE and the model compounds MOC or PAC, the orientation of the sensitizers (DR_A = 2.8 and 1.7 for compounds MOC and PAC, respectively) is low compared to that of EHO-OPPE (DR_A = 8−10). The fact that the orientation of EHO-OPPE in the ternary reference blends is somewhat lower than in a comparable binary reference blend of EHO-OPPE/UHMW PE (see Table 3) is consistent with results obtained on a variety of ternary blends[4] and may be explained by the plasticizing effect of the sensitizer on EHO-OPPE. The latter apparently reduces the efficiency of the orientation process.

Table 3. Photophysical Properties of Uniaxially Oriented Binary and Ternary Blend Films[a]

	DR_A (λ [nm])[b]	DR_A (440 nm)[c]	DR_E [d]
COU-OPPE	4 (320)	2.5	2.2
ANT1-OPPE	1.5 (365)	8	17
ANT2-OPPE	1.5 (365)	6	15.5
EHO-OPPE	n.a.[f]	>25[e]	22
EHO-OPPE/MOC	2.8 (320)	10.5	11.5
EHO-OPPE/PAC	1.7 (365)	8	8.5
MOC	1.8 (320)	n.a.[f]	1.5
PAC	1.1 (365)	n.a.[f]	1.1

[a] All films are uniaxially oriented blends of UHMW PE comprising 2% w/w of the respective guest and are characterized by a draw ratio of ∼70−80 and a final thickness of ∼2 μm. [b] Dichroic ratio in absorption, measured at the indicated wavelength that corresponds to the absorption maximum of the sensitizer employed. [c] Dichroic ratio in absorption, measured at 440 nm, where the absorption is mainly caused by the PPE backbone. [d] Dichroic ratio in emission, measured under isotropic excitation at 440 nm. [e] Measured at 487 nm. [f] n.a. = not applicable.

The orientation of the ANT1-OPPE backbone in the binary blend is comparable to that of EHO-OPPE after tensile deformation, as evidenced by the high dichroic ratio in emission (DR_E = 17 vs 22 for ANT1-OPPE and EHO−OPPE, respectively). The pendent anthracene moiety was barely oriented (DR_A = 1.5 at 365 nm), which makes this an outstanding chromophore for application in polarizing energy transfer processes (see below). Interestingly, the orientation behavior of ANT2-OPPE is similar to that of ANT1-OPPE, which indicates that the orientation of these polymers during deformation is not dominated by the molecular weight of the polymer. To our initial surprise, COU-OPPE hardly oriented during uniaxial drawing (DR_A = 2.5 and DR_E = 2.2). This observation may be rationalized by the previously discussed thermal behavior of the novel polymers. We observed (see above) that the mobility of COU-OPPE between 100 and 120 °C (i.e., at the drawing temperature) was indeed very low. By contrast, ANT-OPPE attains mobility starting from 50 °C, as evidenced by polarization microscopy. Therefore, under the experimental conditions applied, COU-OPPE was not in a mobile phase and, thus, inefficiently oriented, if at all, in tensile deformation. Attempts to orient COU-OPPE in plasticized blends, as well as in blends with ultrahigh molecular weight polypropylene—which can be processed at higher temperatures—currently are in progress.

Polarizing Energy Transfer of COU-OPPE and ANT-OPPE in Oriented PE Films. The presence of energy transfer in binary blends based on COU-OPPE/UHMW PE and ANT-OPPE/UHMW PE, as well as ternary reference blends based on MOC/EHO-OPPE/UHMW PE and PAC/EHO-OPPE/UHMW PE, was confirmed by the absence of donor emission when exciting the samples at 320 or 365 nm for coumarin and anthracene systems, respectively. At these wavelengths,

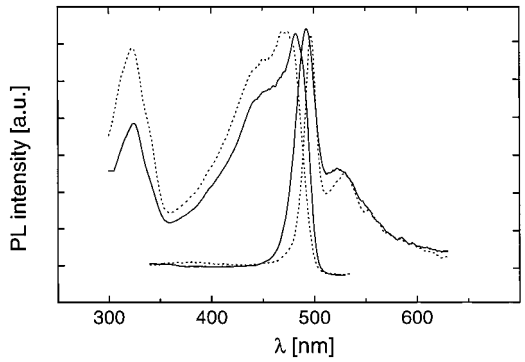


Figure 5. Excitation spectra (normalized) recorded under detection at 580 nm and emission spectra (λ_{ex} = 320 nm) of a binary COU-OPPE/UHMW PE blend film (solid line) and a ternary MOC/EHO-OPPE/UHMW PE blend film (dotted line).

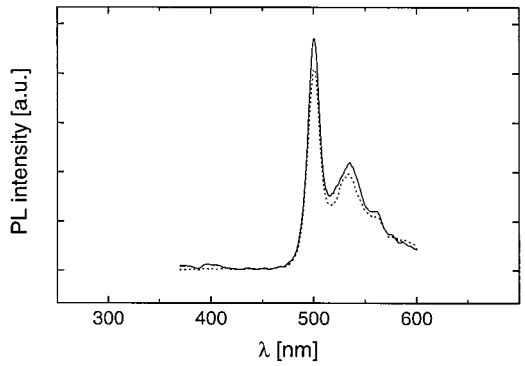


Figure 6. Emission spectra recorded under p-polarized detection and p-polarized (solid lines) or s-polarized (dotted lines) excitation at 365 nm for the ANT-OPPE/UHMW PE blend film.

the absorption spectra are predominantly governed by the sensitizer moieties. At the same time, a strong increase of PPE emission was observed for isotropic excitation of the sample at the absorption maximum of the sensitizer (320 and 365 nm for COU-OPPE and ANT-OPPE, respectively). The emission intensity was found to be comparable to the emission intensity that was observed when exciting the sample at 440 nm. This finding is in strong contrast to the EHO-OPPE/UHMW PE reference blend that showed a significantly lower emission intensity when excited at 320 or 365 nm compared to 440 nm due to the lower absorption at these shorter wavelengths.[4a] In the case of the COU-OPPE/UHMW PE and MOC/EHO-OPPE/UHMW PE systems, the occurrence of energy transfer was further corroborated by excitation scans under detection at 580 nm which revealed a prominent peak at ~320 nm. Excitation and emission scans for blends based on COU-OPPE/UHMW PE and MOC/EHO-OPPE/UHMW PE are given in Figure 5. For the same reasons as discussed already above for the solutions, excitation scans are not reliable for confirming the presence of energy transfer in the case of PPE/anthracene-based blends.

The *polarizing* nature of the energy transfer process is demonstrated for the ANT1-OPPE/UHMW PE blend by the results given in Figure 6. PL spectra of the binary blend ANT1-OPPE/UHMW PE were recorded under p-polarized detection and excitation at 365 nm with p- and s-polarized light. The intensity of p-polarized emission from the blend was found to virtually not depend on the polarization direction of the incident light (when excited at 365 nm). In fact, the ratio of the emission intensities for excitation with p- and s-polarized light (~1.1) is in gratifying agreement with the dichroic ratio in absorption of the film at 365 nm (DR_A = 1.5).

The necessity of having a high degree of orientation of the PPE backbone, together with an essentially isotropic absorption of the sensitizer in order to obtain highly polarized energy transfer, is demonstrated in the COU-OPPE/UHMW PE system which, as already illustrated in Table 3, behaved rather unfavorably. Indeed, the energy transfer was found to be of little polarizing nature.

Finally, the benefit of covalently attaching sensitizers to the PPE backbone was evaluated by comparing the efficiency of polarizing energy transfer in the binary ANT1-OPPE/UHMW PE blend with its ternary reference blend PAC/EHO-OPPE/UHMW PE. On the basis of the isotropic absorption of PAC in the blend, together with a high degree of orientation of EHO-OPPE, the energy transfer was expected to be highly polarizing as well. This, indeed, proved to be the case, although the process is slightly less efficient, which is directly related to the somewhat less favorable dichroic ratio in absorption of PAC in the blend (DR_A = 1.7). The ratio of emission intensities for excitation at 365 nm with p- and s-polarized light under p-polarized detection was around 1.6.

Discussion. The choice of the monomers used here allows for an accessible and a versatile synthesis of PPE polymers with pendent functional groups. Of course, the introduction of sensitizers to the PPE backbone strongly influences the chemical and physical properties of the resulting polymers. For example, the limited molecular weight of our COU-OPPE is principally due to reduced solubility factors as the polymer precipitated during polymerization. Problems related to solubility might be circumvented by using less monomers with pendent sensitizers or by introducing branching in the side chains of the diethynyl monomer.[22]

We have previously shown that a number of prerequisites have to be fulfilled to enable energy transfer from a sensitizer to the PPE backbone.[4] Crucial is the requirement that the photophysical properties of sensitizer and emitter are compatible; i.e., the sensitizer emission spectrum has to overlap with the absorption of the PPE backbone. This condition has been fulfilled in both the coumarin and anthracene systems, as evidenced by the high energy transfer efficiencies (around 80%). Furthermore, close proximity between the donor and the acceptor also is a prerequisite. As evidenced by our results, the spacer length used in this work is in accordance with this requirement, since in both dilute solution and the solid state an efficient energy transfer is observed from the sensitizer to the PPE backbone.

The introduction of pendent, voluminous sensitizers to the polymer backbone leads to a different thermal behavior when compared to the parent unsubstituted EHO-OPPE. As a result, the orientation of the polymer backbone during tensile deformation may be also affected. This is clearly illustrated when the behavior of COU-OPPE is compared to that of ANT1-OPPE: despite the fact that the molecular weights and aspect ratios of these polymers are comparable, the COU-OPPE backbone barely orients during deformation. The lack of mobility of COU-OPPE around the processing temperature is likely to account for this behavior. Such problems may, of course, be solved by, for example, introducing plasticizing agents. If, on the other hand,

the phase behavior of the new polymers is compatible with the orientation process, excellent results are obtained as demonstrated by the dichroic ratios obtained for the ANT-OPPE-based systems.

We have previously shown that *polarizing* energy transfer in photoluminescent polymer films may be a general phenomenon if appropriate materials are adequately combined.[4b] Key requirement is that the luminescent polymer backbone is highly oriented within the film—giving rise to highly anisotropic emission—and that the sensitizer absorbs light isotropically. This proves to be the case in binary as well as ternary blends of the anthracene systems studied (see Table 3). Covalently attaching sensitizers is, therefore, not necessarily a prerequisite for this requirement. However, conjugated polymers with covalently attached senstizers do offer substantial advantages and degrees of freedom with respect to their phase behavior in polymer blends. For example, upon dilution of the presented ternary anthracene-based reference system, the efficiency of energy transfer is expected to diminish. This decrease in energy transfer efficiency has been demonstrated previously for similar blends of UHMW PE, EHO-OPPE, and a coumarin sensitizer.[4b] By contrast, dilution should not affect the energy transfer efficiency when sensitizers are covalently attached to the PPE backbone. We, therefore, qualitatively compared the efficiency of energy transfer occurring in a more diluted binary blend of ANT1-OPPE in UHMW PE with its ternary reference blend (PAC/EHO-OPPE/UHMW PE), when only 0.2% w/w of polymer and/or sensitizer are comprised in the UHMW PE matrix. Figure 7a,b shows the emission spectra obtained under isotropic excitation at 365 nm and p- and s-polarized detection of the diluted binary and ternary anthracene-based blends. The total absence of anthracene emission in the spectra of the binary blend (Figure 7a) and the significant contribution of anthracene emission in the ternary reference blend in both p- and s-polarized detected spectra (Figure 7b) are a clear indication for a reduced energy transfer efficiency in the latter. In addition, the polarizing nature of the energy transfer was found to be concentration dependent as well, as was demonstrated for the ternary PAC/EHO-OPPE/UHMW PE blend. By contrast, the polarizing nature of the energy transfer was virtually not affected by lowering the concentration in the ANT1-OPPE/UHMW PE blend, as evidenced by the comparable ratios of p-polarized emission intensity for p- and s-polarized excitation at 365 nm.

Conclusions

In conclusion, we have developed a novel class of substituted PPE polymers with sensitizers covalently attached to the conjugated polymer backbone. The choice of the starting materials allows for a versatile synthesis and, as a result, easy variation of the pendent sensitizers. Both polymers COU-OPPE and ANT-OPPE show efficient energy transfer in solution from the sensitizer to the polymer backbone with transfer efficiencies around 80%. Furthermore, the phase behavior of ANT-OPPE was found to satisfy the prerequisites necessary to obtain a high degree of *polarizing* energy transfer in polymer films. A high orientation of the PPE backbone together with nearly isotropic absorption of the anthracene sensitizer and an efficient energy transfer process lead to state-of-the-art *polarizing* energy transfer.

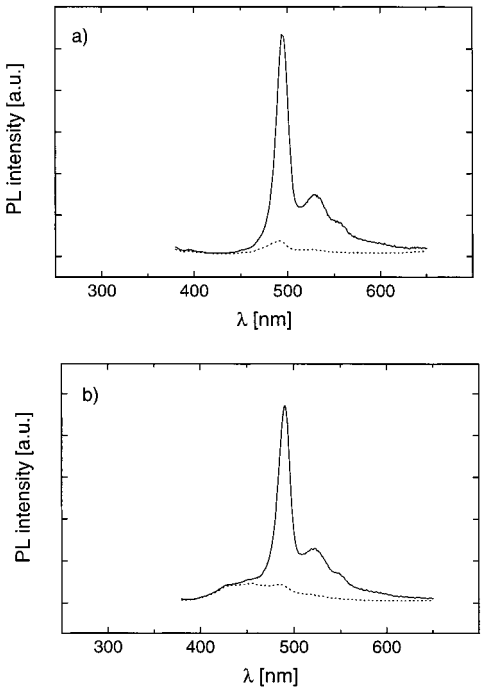


Figure 7. Emission spectra recorded with p-polarized (solid lines) and s-polarized (dotted lines) detection under isotropic excitation at 365 nm of (a) 0.2% w/w ANT-OPPE/UHMW PE blend film and (b) 0.2% w/w PAC/EHO-OPPE/UHMW PE blend film.

Experimental Procedures

Materials. All reagents and solvents were purchased from Aldrich Chemical Co., Fluka, or Acros. Spectroscopic grade $CHCl_3$ (Aldrich, stabilized with EtOH) was used for all absorption and emission experiments. Dimethylformamide (DMF), tetrahydrofuran (THF), and dichloromethane were purchased as dry solvents, stored over molecular sieves, and used as received. Triethylamine (TEA) was dried over KOH and distilled under argon atmosphere. Diisopropylamine was dried over KOH, and toluene was dried over CaH. Both solvents were then distilled under argon atmosphere and deoxygenated by sparging with argon for 1 h. 1,4-Dimethoxy-2,5-diiodobenzene,[11a] 1,4-dihydroxy-2,5-diiodobenzene (**1**),[11a] 1,4-diethynyl-2,5-bis(octyloxy)benzene (**3**),[16] and propyl 9-anthracenecarboxylate (PAC)[18] were synthesized according to previously described procedures. Preparations for the polymerizations were carried out in a glovebox, and all polymerizations were conducted using standard vacuum-line techniques. Blend films were prepared by casting a solution of the appropriate PPE (10 mg), sensitizer (10 mg), and UHMW PE (Hostalen Gur 412, Hoechst, 500 mg) in *p*-xylene (50 g) (dissolution at 130 °C, after degassing the mixture in a vacuum at room temperature for 15 min) into a Petri dish (diameter = 11 cm). The resulting gel was dried under ambient conditions. The films were drawn around 120 °C to draw ratios between 70 and 80.

Methods. ^{1}H NMR and ^{13}C NMR spectra were taken on various Bruker spectrophotometers (300 or 500 MHz for ^{1}H NMR and 75 or 125 MHz for ^{13}C NMR). All data are expressed in ppm relative to the internal TMS standard. DSC measurements were performed on a Perkin-Elmer DSC 7 under N_2 atmosphere. All melting temperatures (T_m) and glass transition temperatures (T_g) were obtained using DSC, where the peak maximum and onset of the glass transition were taken as T_m and T_g, respectively. Polarization microscopy studies were conducted on a Leica DMRX equipped with a Linkam hot stage. Elemental analysis were carried out by the Microanalysis Laboratory of the Department of Chemistry of the ETH Zürich. UV spectra were taken on a Perkin-Elmer Lambda 900 UV—vis spectrophotometer, equipped with motor-driven Glan-Thompson polarizers when polarized spectra were

recorded. Steady-state PL spectra were recorded on a SPEX Fluorolog 3 (model FL312), which were also fitted with motor-driven Glan-Thompson polarizers and with a 450 W Xe lamp for excitation. Relative quantum efficiencies and energy transfer efficiencies were obtained after sparging the $CHCl_3$ solutions with argon for 1 h. The relative quantum efficiency of the novel polymers was subsequently calculated using the previously measured value of 0.85 for EHO-OPPE[16] as the reference absolute quantum efficiency. Polarized UV spectra and PL spectra of the oriented films were taken by sandwiching a piece of the film between quartz slides. A small amount of silicon oil was added to minimize scattering effects at the film surface. The values for DR_A in all binary and ternary blend films were determined after subtracting the scaled absorption spectrum of a pure UHMW PE film of comparable draw ratio from the spectrum of the former. The PL spectra were integrated after smoothing (Savitsky-Golay, nine points) and baseline correction in order to evaluate the dichroic ratios in emission. GPC measurements were performed on a Shimadzu LC10 AT with $CHCl_3$ as eluent. A PL gel 1×10^4 Å with 5 μm particles column was used which was calibrated between 1000 and 500 000 amu with polystyrene standards. For detection, a UV detector (Linear 205) at $\lambda = 254$ nm was used.

6-{4-[(6-Hydroxyhexyl)oxy]-2,5-diiodophenoxy}-1-hexanol (2). The procedure for the preparation of compound **2** was an adaptation from the preparation of 1,4-bis[2-(2-hydroxyethoxy)ethoxy]benzene.[27] To a stirred suspension of K_2CO_3 (7 g) in dry DMF (22 mL) under argon atmosphere was added 1,4-dihydroxy-2,5-diiodobenzene (2 g, 5.52 mmol) in dry DMF (15 mL). After stirring for 15 min, 1-bromohexanol (3 mL) was added dropwise. The mixture was stirred at 75 °C for 3 days and then poured into ice water (300 mL). The aqueous layer was extracted with diethyl ether (3 × 200 mL), and the combined organic layers were washed with diluted HCl, water, and saturated NaCl solution. The organic layers were dried with $MgSO_4$, filtered, and evaporated in vacuo. The crude product was purified by column chromatography (SiO_2; eluent CH_2Cl_2/CH_3CN 4/1; $R_f = 0.18$). The resulting oil was dissolved in CH_2Cl_2 (10 mL); hexane (10 mL) was added, and the solution was refrigerated overnight. Pure **2** was then obtained as a white powder (1.21 g, 39%). $T_m = 83$ °C. ^{1}H NMR ($CDCl_3$): δ 7.17 (s, 2H, H-ortho); 3.93 (t, 4H, CH_2OAr); 3.65 (t, 4H, CH_2OH); 1.84 (qui, 4H, CH_2CH$_2$OAr); 1.50 (qui, 4H, CH_2CH$_2$OH); 1.30 (m, 8H, CH_2); 1.13 (bs, 2H, OH).^{13}C NMR ($CDCl_3$): δ 152.8, 122.8, 86.3 (aromatic carbons); 70.2, 62.9, 32.6, 29.1, 25.9, 25.4 (aliphatic carbons). Anal. Calcd for $C_{18}H_{28}I_2O_4$ (562.23): C, 38.45; H, 5.02; O, 11.38. Found: C, 38.65; H, 4.98; O, 11.55.

7-({6-[2,5-Diiodo-4-({6-[(4-methyl-2-oxo-2*H*-7-chromenyl)oxy]hexyl}oxy)phenoxy]hexyl}oxy)-4-methyl-2*H*-2-chromenone (4a). The procedure for the preparation of **4a** was adapted from ref 17. To a stirred solution of **2** (380 mg, 0.67 mmol), 7-hydroxy-4-methylcoumarin (250 mg, 1.42 mmol), and PPh_3 (535 mg, 2.0 mmol) in dry THF (8 mL) was slowly added a solution of diethylazodicarboxylate (352 mg, 2.0 mmol) in dry THF (2 mL). The solution was stirred under argon atmosphere for 18 h at ambient temperature. THF was removed in vacuo, and the oily residue was dissolved in $CHCl_3$ (5 mL). The organic layer was extracted with water and saturated NaCl solution, dried with $MgSO_4$, filtered, and evaporated in vacuo. The resulting oil was purified using column chromatography (SiO_2; eluent CH_2Cl_2/EtOAc 94/6; $R_f = 0.25$), giving **4a** as a white powder. The product was further purified by dissolving in CH_2Cl_2 and adding an equal amount of hexane until a white powder slowly precipitated (283 mg, 46%). $T_m = 170.0$ °C. ^{1}H NMR (CD_2Cl_2): δ 7.53 (d, 2H, H-5); 7.21 (s, 2H, H-ortho); 6.88 (d, 2H, H-6); 6.81 (s, 2H, H-8); 6.08 (s, 2H, H-3); 4.13 (t, 4H, CH_2O-cou); 3.96 (t, 4H, CH_2OAr); 2.39 (s, 6H, CH_3); 1.87 (q, 4H. CH_2CH$_2$O); 1.68 (t, 8H, CH_2). ^{13}C NMR (CD_2Cl_2): δ 162.2 (C═O); 160.9, 155.3, 152.8, 152.6, 125.6, 122.7, 113.4, 112.4, 111.7, 101.2, 86.1 (aromatic carbons); 70.1; 68.5; 29.0; 28.9; 25.7; 25.5; 18.4 (aliphatic carbons). Anal. Calcd for $C_{38}H_{40}I_2O_8$ (878.54): C, 51.95; H, 4.59; O, 14.57. Found: C, 51.88; H, 4.56; O, 14.33.

4-Methyl-7-(octyloxy)-2*H*-2-chromenone (MOC). The procedure for the preparation of MOC was adapted from ref 17. To a stirred solution of octanol (370 mg, 2.83 mmol), 7-hydroxy-4-methylcoumarin (500 mg, 2.83 mmol), and PPh_3 (1.11 g, 4.25 mmol) in dry THF (20 mL) was slowly added a solution of diethylazodicarboxylate (740 mg, 4.25 mmol) in dry THF (5 mL). The solution was stirred under argon atmosphere for 18 h at ambient temperature. The precipitate was filtered off, and the filtrate was evaporated in vacuo. The resulting oil was purified using column chromatography (SiO_2; eluent CH_2Cl_2/hexane 1/1, $R_f = 0.15$) and yielded a colorless oil (0.66 g, 77%) that slowly solidified upon standing. ^{1}H NMR ($CDCl_3$): δ 7.53 (d, 1H, H-5); 6.87 (d, 1H, H-6); 6.83 (s, 1H, H-8); 6.15 (s, 1H, H-3); 3.96 (t, 2H, CH_2O); 2.43 (s, 3H, CH_3); 1.89 (qui, 2H. CH_2CH$_2$O); 1.68 (m, 2H, CH_2CH$_2$CH$_2$O). 1.50 (bs, 8H, $(CH_2)_4$); 0.92 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 162.2 (C═O); 161.4, 155.3, 152.6, 125.4, 113.4, 112.7, 111.8, 101.3 (aromatic carbons); 68.6, 31.8, 29.3, 29.2, 29.0, 26.0, 22.6, 18.6, 14.1 (aliphatic carbons). Anal. Calcd for $C_{18}H_{24}O_3$ (288.39): C, 74.97; H, 8.39; O, 16.64. Found: C, 74.99; H, 8.25; O, 16.69.

COU-OPPE. Compound **3** (93.2 mg, 0.243 mmol), **4a** (203 mg, 0.223 mmol), iodobenzene (12 mg, 0.058 mmol), $Pd(PPh_3)_4$ (12.3 mg), and CuI (9 mg) were added to a mixture of toluene (7 mL) and diisopropylamine (3 mL). Immediately after the mixture was placed in an oil bath heated to 75 °C, a yellow precipitate started to appear. Nevertheless, the mixture was stirred for 18 h at 75 °C. An additional amount of iodobenzene (0.05 mL) was added, and the suspension was stirred for another 2 h. The resulting, strongly luminescent suspension was precipitated into MeOH (200 mL), and the yellow precipitate was filtered over a glass filter (P4). The yellow solid was dissolved in $CHCl_3$ (3 mL) and reprecipitated into MeOH (300 mL). The collected solid was thoroughly washed with MeOH and dried in vacuo (100 mg, 44%). $T_{m,dec} = 157$ °C. ^{1}H NMR (CD_2Cl_2): δ 7.60 (bs, phenyl end group); 7.54 (d, 2H, H-5); 7.45 (bs, phenyl end group); 7.05 (d, H-ortho); 6.83 (d, H-6); 6.77 (s, H-8); 6.05 (s, H-3); 4.09 (m, CH_2OAr); 2.39 (s, CH_3-cou); 1.87−1.25 (m, CH_2); 0.85 (t, CH_3). ^{13}C NMR ($CDCl_3$): δ 162.1 (C═O); 161.8 (cou); 155.3 (cou); 153.5 (Ar−O); 152.5 (cou); 131.5 (Ph end group); 128.3 (Ph end group); 125.5 (cou); 117.2 (Ar−H); 114.4 (Ar−C≡); 113.4 (cou); 112.5 (cou); 111.8 (cou); 101.4 (cou); 91.6 (C≡C); 69.7, 69.5, 68.4 (OCH_2); 31.8, 29.4−29.0 (5×), 26.0−25.8 (3×), 22.6 (CH_2); 18.6 (CH_3-cou); 14.1 (CH_3). Anal. Calcd for $C_{64}H_{76}O_{10}$ (1005.29): C, 76.47; H, 7.62. Found: C, 74.90; H, 7.64.

6-[4-({6-[(9-Anthrylcarbonyl)oxy]hexyl}oxy-2,5-diiodophenoxy]hexyl 9-Anthracenecarboxylate (4b). The procedure for the preparation of **4b** was adapted from ref 18. 9-Anthracenecarboxylic acid (250 mg, 1.12 mmol) was suspended in dry CH_2Cl_2 (5 mL). Trifluoroacetic anhydride (0.7 mL) was added slowly via a syringe, and the suspension slowly turned into a yellow solution. After stirring for 15 min, a solution of **2** (300 mg, 0.53 mmol) in CH_2Cl_2 (9 mL) was slowly added. The solution was stirred overnight at ambient temperature. After evaporation of the solvent, the resulting yellow oil was purified using a filtration over SiO_2 (eluent: CH_2Cl_2). Recrystallization from toluene/heptane 1/1 afforded off-white crystals (365 mg, 70%). $T_m = 148.7$ °C. ^{1}H NMR ($CDCl_3$): δ 8.56 (s, 2H, H-10); 8.05 (m, 8H, H-1 + H-4); 7.50(m, 8H, H-2 + H-3); 7.16 (s, 2H, H-ortho); 4.64 (t, 4H, CH_2OCO); 3.91 (t, 4H, CH_2OAr); 1.93 (q, 4H, CH_2CH$_2$OCO); 1.83, CH_2CH$_2$OAr); 1.58 (m, 8H, CH_2). ^{13}C NMR ($CDCl_3$): δ 169.7 (C═O); 152.8, 131.0, 129.2, 129.0, 128.6, 128.4, 128.0, 126.9, 125.0, 122.8, 86.3 (aromatic carbons); 70.1; 65.8; 29.0; 28.7; 25.8 (2 × CH_2) (aliphatic carbons). Anal. Calcd for $C_{48}H_{44}I_2O_6$ (970.68): C, 59.39; H, 4.57; O, 9.89. Found: C, 59.59; H, 4.37; O, 9.89.

Propyl 9-Anthracenecarboxylate (PAC). PAC was prepared according to a previously described procedure.[18] Recrystallization from MeOH afforded light yellow crystals (0.75 gr, 62%). $T_m = 75$ °C (lit.[18] 68−69 °C). ^{1}H NMR ($CDCl_3$): δ 8.51 (s, 1H, H-10); 8.04 (m, 4H, H-1 + H-4); 7.53 (m, 4H, H-2 + H-3); 4.59 (t, 2H,CH_2OCO); 1.94 (q, 2H, CH_2CH_2OCO); 1.08 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 169.7 (C═O); 131.0, 129.2, 128.6, 128.4, 128.2, 126.9, 125.2, 125.0 (aromatic carbons); 67.4; 22.2, 10.6 (aliphatic carbons). Anal. Calcd for $C_{18}H_{16}O$

(264.32): C, 81.79; H, 6.10; O, 12.11. Found: C, 81.70; H, 6.31; O, 12.21.

ANT1-OPPE. Compound **3** (87.5 mg, 0.228 mmol), **4b** (192 mg, 0.197 mmol), iodobenzene (14 mg, 0.067 mmol), $Pd(PPh_3)_4$ (28 mg), and CuI (20 mg) were added to a mixture of toluene (8 mL) and diisopropylamine (3 mL). The mixture was stirred at 75 °C for 18 h. An additional amount of iodobenzene (0.05 mL) was added, and the suspension was stirred for another 2 h. The resulting strongly luminescent suspension was precipitated into MeOH (300 mL), and the yellow precipitate was filtered over a glass filter (P4). The solid precipitate was dissolved in $CHCl_3$ (4 mL) and reprecipitated into MeOH (300 mL). The yellow solid was thoroughly washed with MeOH and dried in vacuo (130 mg, 60%). T_g = 44.8 °C. ^{1}H NMR (CD_2Cl_2): δ 8.52 (s, H-10); 8.05 (t, H-1 + H-4); 7.50 (m, H-2 + H-3 + phenyl end group); 7.36 (s, phenyl end group); 7.01 (d, H-ortho); 4.57 (m, CH_2OCO); 3.93 (m, CH_2OAr); 1; 1.89−1.25 (m, CH_2); 0.85 (t, CH_3). ^{13}C NMR ($CDCl_3$): δ 169.6 (C═O); 153.6 (Ar−O); 131.6 (Ph end group); 131.0 (ant); 129.2 (ant); 128.6 (ant); 128.4 (ant); 128.3 (Ph end group); 128.1 (ant); 126.9 (ant); 125.4 (ant); 124.9 (ant); 117.4 (Ar−H); 114.4 (Ar−C≡); 91.6 (C≡C); 69.7, 69.5, 65.7 (OCH_2); 31.8, 29.4−29.2 (4×), 28.8, 26.1, 25.9, 25.7, 22.6 (CH_2); 14.1 (CH_3). Anal. Calcd for $C_{74}H_{80}O_8$ (1097.44): C, 80.99; H, 7.35. Found: C, 78.93; H, 7.37.

ANT2-OPPE. Compound **3** (86.3 mg, 0.225 mmol), **4b** (199.8 mg, 0.206 mmol), iodobenzene (8 mg, 0.067 mmol), $Pd(PPh_3)_4$ (12 mg), and CuI (25 mg) were added to a mixture of toluene (8 mL) and diisopropylamine (3 mL). The reaction and workup procedure were conducted comparable as described for ANT1-OPPE (160 mg, 70%). T_g = 42.9 °C. ^{1}H NMR (CD_2Cl_2): δ 8.52 (s, H-10); 8.05 (t, H-1 + H-4); 7.50 (m, H-2 + H-3 + phenyl end group); 7.36 (s, phenyl end group); 7.01 (d, H-ortho); 4.57 (m, CH_2OCO); 3.93 (m, CH_2OAr); 1; 1.89−1.25 (m, CH_2); 0.85 (t, CH_3). ^{13}C NMR ($CDCl_3$): δ 169. (C═O); 153.6 (Ar−O); 131.0 (ant); 129.2 (ant); 128.6 (ant); 128.4 (ant); 128.1 (ant); 126.9 (ant); 125.5 (ant); 124.9 (ant); 117.4 (Ar−H); 114.5 (Ar−C≡); 69.7, 69.5, 65.7 (OCH_2); 31.8, 29.4−29.2 (4x), 28.8, 25.9 (2×), 25.7, 22.6 (CH_2); 14.1 (CH_3). Anal. Calcd for $C_{74}H_{80}O_8$ (1097.44): C, 80.99; H, 7.35. Found: C, 75.04; H, 7.65; I, 1.52.

EHO-OPPE. The polymer was prepared according to a previously described procedure.[16] Anal. Calcd for $C_{48}H_{72}O_4$ (713.11): C, 80.85; H, 10.18. Found: C, 80.59; H, 9.98.

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