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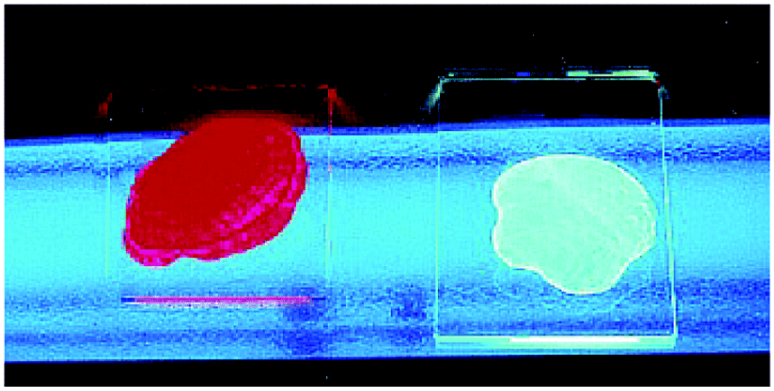

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Attaching Perylene Dyes to Polyfluorene: Three Simple, Efficient Methods for Facile Color Tuning of Light-Emitting Polymers

Christophe Ego, Dirk Marsitzky, Stefan Becker, Jingying Zhang,
Andrew C. Grimsdale, Klaus Müllen,* J. Devin MacKenzie, Carlos Silva, and
Richard H. Friend

*Contribution from the Max-Planck-Institut für Polymerforschung, Ackermannweg 10,
55128 Mainz, Germany and Cavendish Laboratory, University of Cambridge, Madingley Road,
Cambridge CB3 0HE, United Kingdom*

Received April 22, 2002; E-mail: muellen@mpip-mainz.mpg.de

Abstract: The emission color of fluorene-based polymers can be facilely tuned across the whole visible spectrum by copolymerization with perylene dyes. Methods are demonstrated for incorporation of the dyes in the polymer mainchain, at the chain termini, or as side chains. Efficient energy transfer causes the emission to come solely from the dye units. Efficient LEDs have been made from the copolymers with dyes in the mainchain.

Introduction

Polymer light-emitting diodes (PLEDs) have been the subject of intense academic and industrial research interest since their discovery in 1989[1] and are now emerging as commercial products. The main advantages of electroluminescent conjugated polymers as compared with inorganic or molecular organic materials for LEDs are lower production costs, high flexibility, readier processability, the possibility of uniformly covering large areas by inexpensive solution processing techniques such as spin coating, and the many ways to fine-tune their optical and electrical properties by varying the structure.[2] In this paper, we present three simple new methods for tuning the emission color of light-emitting polymers across the entire visible spectrum.

To achieve a full color flat-panel display, red, green, and blue light-emitting polymers with narrow emitting spectra are required. Further material requirements are good processability, high luminescence efficiencies with low turn on and operating voltages, and good chemical and electrical stability as well as photostability. Color tuning conjugated polymers may be achieved by substitution (e.g., alkyl or alkoxy substitution of PPV changes the emission color from green to red-orange[2]) by controlling the effective conjugation length[3] or by blending with another emissive material. If two materials with different band gaps (and hence different emission colors) are mixed together, then energy transfer from the higher to the lower band gap material may occur leading to emission solely or predominantly from the latter. One method for color tuning is thus to blend a dye chromophore into a polymer matrix; for example, the blending of red-emitting tetraphenylporphyrin into a blue-emitting polyfluorene has been used to obtain a red-emitting LED.[4]

Though such blending has the advantage of being easy to do and enables one to take advantage of the wide range of commercially available dyes, blends of polymers and dyes have a tendency to show phase separation over time, which leads to instability in the device's performance. Our new solution to this problem is to covalently attach the dye to the polymer. The significant advantages that this approach has compared with blending are first, that migration of the dye chromophore inside the polymer matrix, which may lead to aggregation and poor device performance, is prevented; and second, that efficient energy transfer to the dye chromophore and the confinement of the singlet excitons in the chromophore therein is facilitated.

We have now achieved effective tuning of the emission color over the whole visible region, by attachment of perylene dyes to polyfluorene chains either as (i) comonomers in the main chain, (ii) as endcapping groups at the chain termini, or (iii) as pendant side groups, by simple high yielding syntheses. These polymers are suitable individually to act as efficient red, green, or blue emitters for full color displays or might be blended to produce other emission colors including pure white light.

Polyfluorenes were chosen as the polymer backbone, owing to their large band gaps, high photoluminescence quantum yields, excellent chemical and thermal stability as well as photostability, good solubility and film-forming properties, and the ready availability from high yielding synthetic routes of well-defined high molar-mass polymers.[5] Perylene dyes were chosen as the low band gap chromophores because of their excellent light fastness, high chemical stability, high photoluminescence

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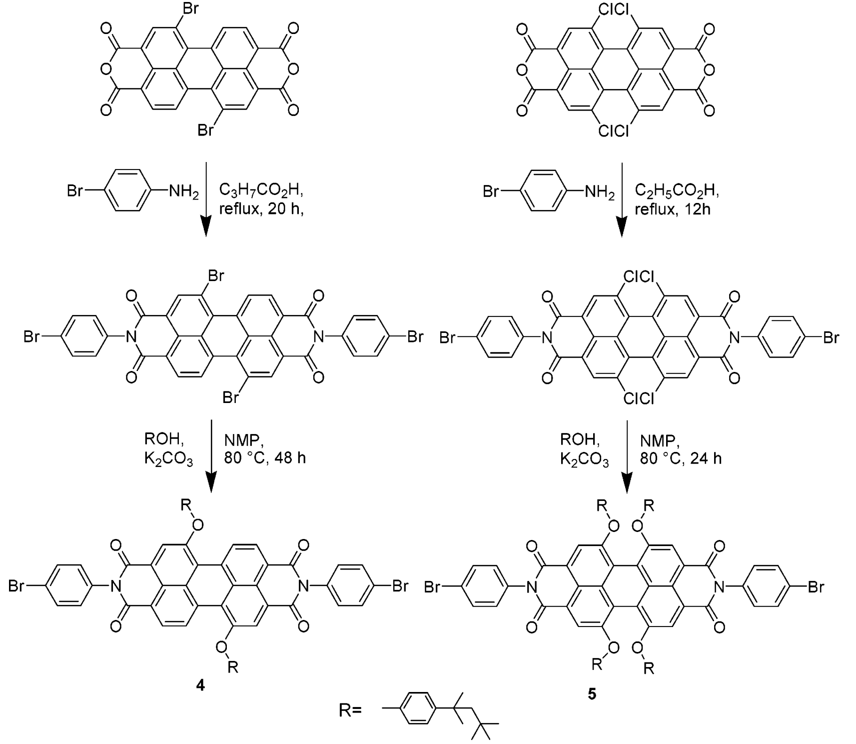
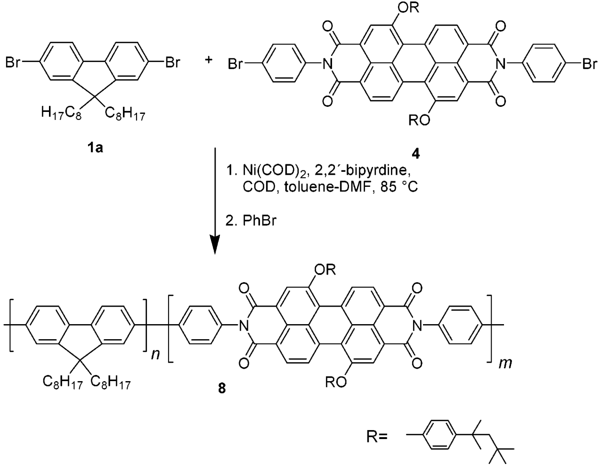
Scheme 1 . Synthesis of Dyes **4** and **5**



Scheme 2 . Copolymerization of Perylene Dyes with Dibromodioctylfluorene



quantum yield, and the large range of colors accessible by variation of the substitution pattern on the perylene core through high yielding synthetic routes.[6]

We thus assembled a “molecular toolbox” of fluorene and perylene monomers which enabled us to prepare copolymers with emission colors covering the visible spectrum in high yielding onepot syntheses.

Results and Discussion

The preparation of the first type of the perylene−fluorene copolymer described previously, that is, with the perylenes as comonomers in the chain, is readily realized by the statistical copolymerization of dibromodialkylfluorene **1** with suitable bisbrominated perylenes (Scheme 2) by nickel(0) mediated polycoupling (Yamamoto polymerization[7]). The comonomers chosen were the dibromoperylene dyes **2**−**5** (Figure 1) with emission maxima at 525 (green), 540 (yellow), 584 (orange), and 626 nm (red-orange). The syntheses of **2**[8] and **3**[9] have previously been published. It should be noted that dyes **2** and **3** consist of inseparable 1:1 mixtures of the 3,9- and 3,10-dibromo isomers, but this has no effect on their optical properties. The dyes **4** and **5** were prepared in high yield, as shown in Scheme 1. Condensations of 1,6,7,12-tetrachloro- and 1,7-dibromo-perylene tetracarboxylic acid anhydride, respectively, with 4-bromoaniline in refluxing butyric or propionic acid gave the diimides, which then underwent nucleophilic susbtitution of the halides in the bay positions with 4-*tert*-octylphenoxide to produce **4** and **5** in overall yields of 60% and 86%, respectively. The copolymers with **2** and **3** retain unbroken conjugation, while the imide units in **4** and **5** interrupt conjugation in their copolymers which might be expected to affect their electrical and optical properties.

Polymerization of a mixture of the appropriate dibromoperylene dye (1−5 wt %) and 2,7-dibromo-9,9-dioctylfluorene **1a** with nickel(0) in DMF−toluene for 24 h, followed by reaction with an excess of bromobenzene to remove any residual terminal bromine functionality (endcapping), was then performed to give the copolymers **6**−**9** (Figure 2) in 62−90% yield, as illustrated in Scheme 2 for the preparation of **7**. The removal of the bromine endgroups is important, as it has been shown that such groups are detrimental to LED device performance.[10]

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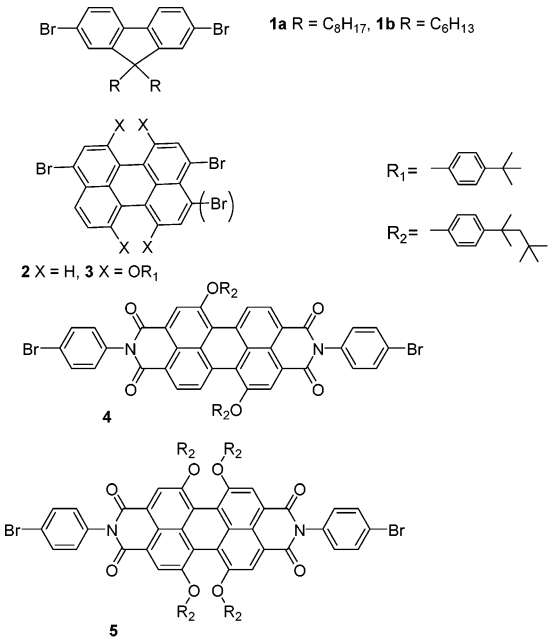

Figure 1. Molecular toolbox for color tuning.

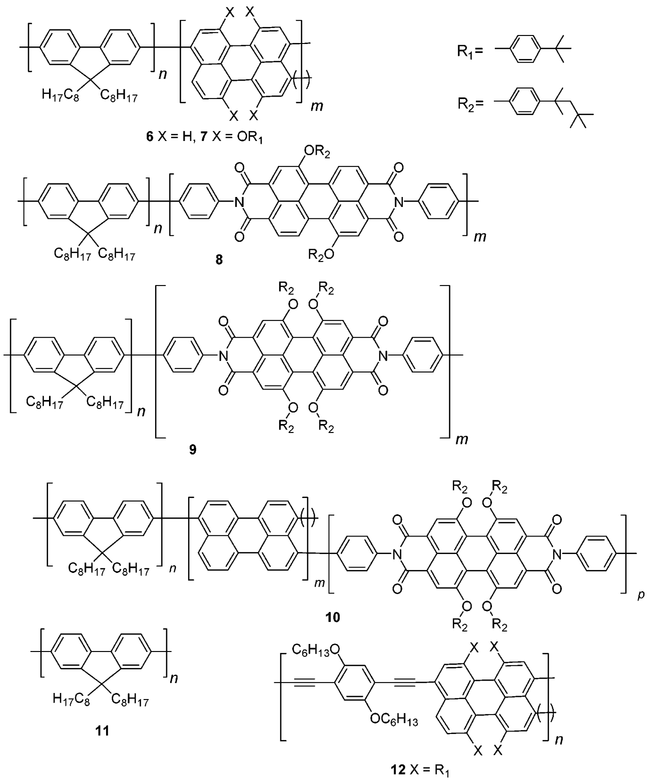

Figure 2. Perylene dye−fluorene mainchain copolymers.

To test the effect of varying the amount of dye on the optical and other properties, copolymer **9** was prepared using 1% and 5% of dye. In the case of the longer wavelength emitting perylenes such as **5**, the overlap of the PF emission and the perylene absorption spectra, as shown in Figure 3, is relatively poor with the absorption of the perylene reaching a maximum at 590 nm, while the emission of the PF segments is centered near 465 nm. The solid-state optical color tuning, though still much stronger than that observed in solution, is not as pronounced as in the case of the copolymers **6** or **7**, which have blue-shifted absorptions. In the case of **7**, the perylene absorption near 470 nm overlaps well with the PF emission and the optically stimulated color tuning effect is nearly complete as the integrated perylene emission intensity is more than 2 orders of magnitude higher than the remaining PF emission. This is consistent with the most general description of resonance energy transfer, where the rate constant of exciton transfer from the donor fluorophore to the acceptor chromophore, k_{DA}, is given in units of inverse picoseconds by[11]

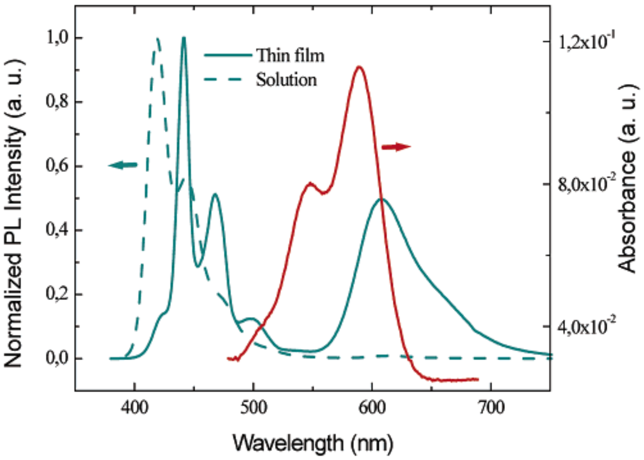

Figure 3. Photoluminescence spectra for **9** in thin film (solid cyan line) and solution (dashed cyan line) and the solid-state absorption spectrum of the perylene **5** (red line).

$$k_{DA} = 1.18 V_{DA}^{2} \int_{0}^{\infty} f_{D}(\bar{\nu}) A_{A}(\bar{\nu}) d\bar{\nu} \qquad (1)$$

within a Fermi golden rule approximation. Here, f_D and A_A are the fluorescence and absorption spectra of the donor and acceptor, respectively, normalized such that the integral over all photon energies is unity. V_{DA}^2 is the energy transfer electronic coupling matrix element between donor and acceptor. Comparison of the degree of spectral overlap between the polyfluorene donor and dyes **2** and **4** showed that the degree of spectral overlap is higher for **2** than for **4**. The spectral overlap derived from eq 1 is 2.1×10^{-4} cm^{-1} for dye **2** but is only 6.1×10^{-5} cm^{-1} for dye **4**. If the electronic couplings between PF and the two dyes are assumed to be similar, the rate constant for energy transfer to dye **2** is thus an order of magnitude higher than that to dye **4**. To explore this issue further, we also made a copolymer **10** containing both **5** and the green-emitting **2** (3% of each) to see if transfer via the green-emitting segments would improve the overall energy transfer to the red-emitting chromophores.

The physical characteristics of the copolymers **6**−**10** and of a sample of the polyfluorene homopolymer **11** prepared using the same reaction conditions are given in Table 1. As can be seen, the copolymers all show high thermal stability with decomposition temperatures above 400 °C by TGA, comparable with the case of the homopolymer. Their molar masses as determined by GPC against polystyrene standards are generally slightly lower than those for the homopolymer with number averaged masses (M_n) of 30−140 000 corresponding to degrees

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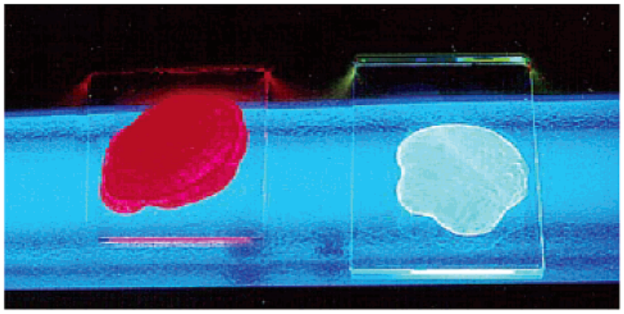

Figure 4. Fluorescence of films of **9** (left) and **11** (right) under UV irradiation.

of polymerization of about 90−400 units and polydispersities (D) of usually around 4. The polydispersities of the copolymers are higher than those for the homopolymer (2.8), which is most readily explained by the reactivity of the bromodyes being lower than that for the bromofluorene, leading to the slower addition of fluorene to a terminal dye unit and greater probability of a chain terminating debromination occurring at such a site. Slightly different M_n and D values were determined, depending upon whether the UV detector in the GPC was set in the range for maximum absorption of the fluorene homopolymer (360−390 nm) or of the attached dye. The values in Table 1 are for detection at the former. It should be noted that the molar masses obtained for rigid rod polymers from GPC against polystyrene standards are known to be frequently too high, with an overestimation factor of 2.7, having been determined for polyfluorenes by comparison of GPC data with more accurate masses determined by light scattering methods.[12] The copolymer **9** had a higher M_n and lower polydispersity when made with 1% rather than with 5% of the dye **5**, suggesting that incorporation of larger amounts of dye might be detrimental to the polymer properties. The copolymers all show excellent solubility in common organic solvents and good film-forming properties.

The absorption and emission spectra of these copolymers in solution show predominantly absorption by and emission from the fluorene units, as might be expected for materials containing only low amounts of the dye chromophores in the absence of energy transfer from the fluorenes to the dyes. However, in the solid state, efficient energy transfer to the chromophores occurs so that the emission is predominantly from the latter, though significant emission is still seen from the fluorene backbone, as illustrated for copolymer **9** in Figure 3.

The efficient intermolecular solid-state energy transfer process in the copolymer can be seen in the dramatic enhancement of the 620 nm perylene emission in thin film (solid cyan line) as compared with the solution spectrum (dashed cyan line). The red line shows the solid-state absorption of the perylene which only partially overlaps the PF emission. Figure 4 shows the fluorescence of films of the copolymer **9** and the homopolymer **11**, illustrating how dramatic is the difference in emission color. The absolute photoluminescence efficiencies (Table 1) were measured from thin films spun on quartz substrates following the method of de Mello et al.[13] The PL efficiencies of the copolymers are lower than those for the homopolymer **11**, with the efficiencies being lowest for the copolymers **8**−**10** where the conjugation in the main chain is interrupted. That the PL efficiency is lowest (33%) for the copolymer **8** may be due to the particularly strong tendency of the chromophore **4** to aggregate. The energy transfer in copolymer **9** appears to be as efficient with 1% of dye as with 5%, showing that large amounts of chromophore are unnecessary for efficient color tuning. The higher PL quantum efficiency in the copolymer with 1% of dye may be due to a lower degree of aggregation of the perylene units in this polymer. The very low (7%) PL efficiency for the copolymer **10** is probably due to aggregation or a similar fluorescence quenching process, as a stepwise energy transfer from fluorene to **2** to **5** should not be less efficient than a direct transfer to **5**.

Table 1. Physical Data for the Polymers **6**−**11**, **14**, and **20**

polymer (% dye)	M_n[a] (g/mol)	D[a]	TGA[b] (°C)	PL efficiency[c] (%)
6 (3%)	47 930	4.1	448	51
7 (5%)	32 300	4.9	443	40
8 (5%)	63 510	3.6	447	33
9 (1%)	142 500	3.8	445	42
9 (5%)	75 210	6.3	445	38
10 (3% + 3%)	46 650	7.7	451	7
11	84 500	2.8	463	56
14	20 730	2.1	453	>60
20	10 430	2.6	454	

[a] Molar mass (M_n) and polydispersity (D) were determined by GPC in THF against polystyrene standards with UV detection set between 360 and 390 nm. [b] TGA data show the temperature for onset of the primary mass loss. [c] PL efficiencies were determined for thin films spun upon quartz by the method of de Mello et al.[13]

Table 2. LED Performance of Polymers **6**−**9** in Devices ITO/PEDOT−PSS/Polymer/Ca−Al

copolymer	external EL efficiency [%]	onset voltage [V]	luminescence [Cd/A]
6	0.6	12	0.9
7	0.2	11	0.4
8	0.5	8	1.6
9	0.3	15	1.4

The polymers **6**−**9** have been tested as emissive materials in LEDs and were found to exhibit good device performance. Data from the nonoptimized LEDs using a poly(styrene sulfonate) doped poly(3,4-ethylenedioxythiophene) (PEDOT/PSS) hole-transporting buffer layer and a calcium−aluminum cathode are shown in Table 2.

The EL spectra show emission only from the dye chromophores (Figure 5). This is presumably because the smaller band gaps of the perylene units cause them to act as traps for the injected charges, leading to effective exciton confinement, which acts to significantly increase the dye to fluorene emission ratios compared with those seen for optical excitation. This is supported by the high electron affinities that have been observed for similar perylenes containing electron-withdrawing diimide bridges.[14] The EL spectra of **6**, **7**, and **9** closely resemble their PL spectra with the omission of the fluorene emission, but the EL emission from **8** is red shifted and broader. Thus, **6** showed bright green EL with a maximum at 520 nm, (CIE x,y coordinates of 0.362,0.555), polymer **7** produced yellow emission with a maximum at 558 nm (x,y = 0.414,0.519), and **9** gave red-orange EL peaking at 600 nm (x,y = 0.590,0.365). The emission from devices using the copolymers **9** and **7** and

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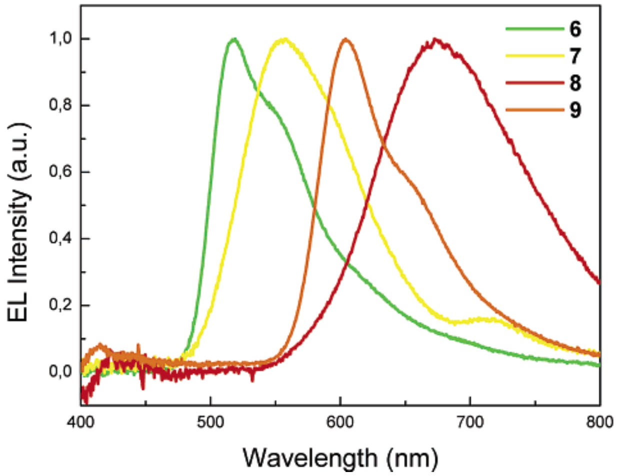

Figure 5. EL spectra of the copolymers **6**−**9** in devices ITO/PEDOT−PSS/polymer/Ca−Al.

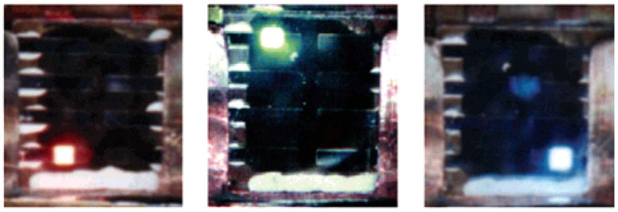

Figure 6. Electroluminescence from devices using polymers **9** (left), **7** (center), and **11** (right).

the homopolymer **11** is shown in Figure 6. The emission from **8** was deep red (CIE $x,y = 0.636,0.338$) with a maximum at 675 nm, which is over 30 nm red shifted from the PL maximum (643 nm). Somewhat surprisingly given its relatively low PL efficiency, the copolymer **8** showed relatively high EL efficiency and luminance and the lowest onset potential of the copolymers. Presumably because the difference in electron affinities between the dye and the fluorene is greatest for the red emitting perylene (~0.4 eV), the charge trapping is particularly efficient in this case.

The enhancement in color tuning is shown clearly by the comparison of the emissions from **9** under optical (Figure 4) and electrical stimulation (Figure 6). The external EL efficiencies of 0.2−0.6% for nonoptimized devices show that these copolymers have considerable potential as emissive materials for full-color displays. The maximum EL efficiencies for the LEDs using **6** (0.9 Cd/A) and **8** (1.6 Cd/A) are higher than those seen for green-emitting PPV derivatives under similar conditions[15,16] and are not greatly inferior to the efficiencies (2−7 Cd/A) of optimized blue- or green-emitting polyfluorene devices using similar electrode materials.[17] The efficiencies for the red-orange-emitting polymers **8** and **9** are an order of magnitude higher than those for the red-orange-emitting copolymer **12** made by the Hagihara polycoupling of **3** with a diethynylbenzene[8] which has a maximum efficiency of only 0.02%.[18a] The devices show stable emission with no significant change in the emission spectra over lifetimes of $>10^3$ s. By contrast, similar devices using a blend of perylene dyes and polyfluorenes showed rapid degradation with the emission intensity dropping to 50% of the original luminance after only 60 s, accompanied by a decrease of an order of magnitude in luminescence efficiency, a change in emission spectra from the perylene toward the fluorene, and a rapid increase in voltage demand, which is explicable in terms of the dye aggregating and forming nonradiative trap sites. As shown in Figure 7, within 15 min the emission from a blend of dye **4** in poly(dioctylfluorene) becomes dominated by the polyfluorene, closely resembling the solution spectrum of the copolymer **8**.

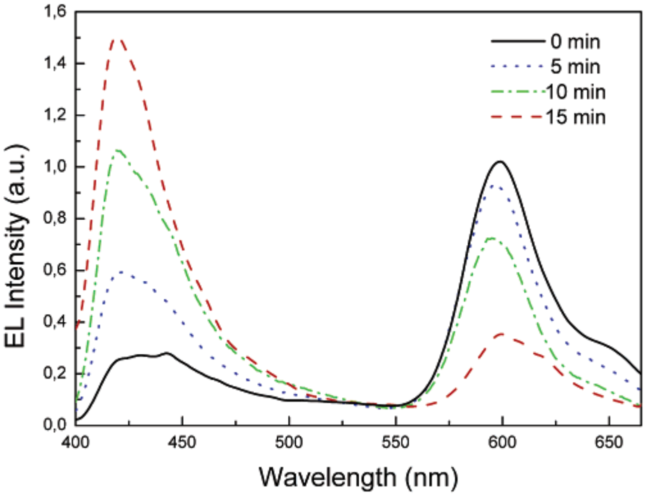

Figure 7. Time-resolved normalized EL spectra of a blend of dye **4** (3 wt %) in polymer **11**.

Given that because of the low concentration of dyes these copolymers should be highly compatible with each other and the homopolymer for blending purposes, it should be possible by blending suitable combinations of these materials to obtain efficient emission with colors covering much of the visible spectrum and even potentially white emission. White emission has been previously achieved by us by blending **12** with a blue-emitting polymer.[18]

The second type of polymer is made by the same synthetic procedure as that described previously but using a monobrominated perylene derivative (Scheme 3). As addition of this to the growing polymer chain acts as a terminating (endcapping) step, the polymers so obtained contain perylene units only at the end of the polymer. As the dyes are only found at the end of the chains, these polymers are more suitable for studying the physics of energy transfer between the fluorene and the dye units than the polymers described in the previous section, in which the dyes are randomly distributed throughout the material. This method also permits control of the M_n and hence the physical properties, including film-forming abilities, of the resulting polymers by varying the ratio of monomer to endcapper, as has been demonstrated by Scherf et al. for polyfluorenes with triarylamine endcappers.[19] As the chain can also be

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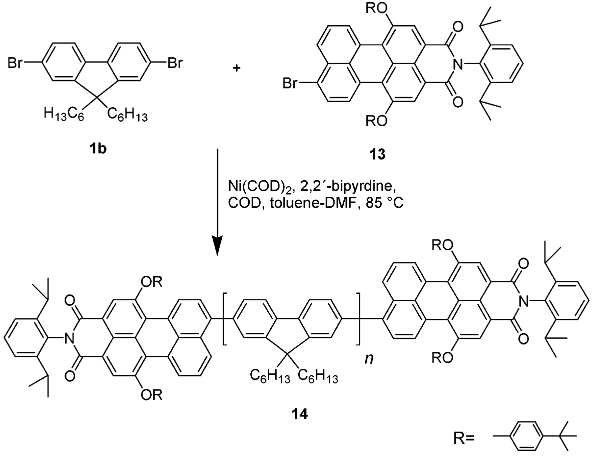
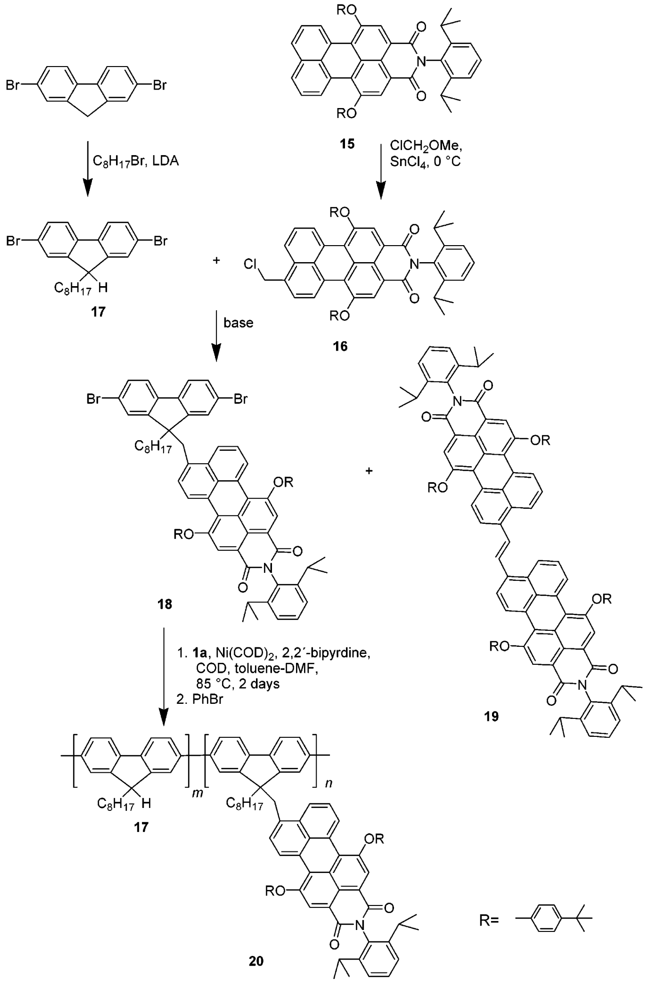
Scheme 3**.** Synthesis of a Perylene-Endcapped Polyfluorene



Scheme 4**.** Synthesis of Copolymer **20** with Pendant Perylene Dye Groups



terminated by reaction of the intermediate aryl-nickel species with a proton leading to endcapping with a hydrogen, the concentration of the endcapping groups is slightly less than the theoretical value from the proportion of endcapper in the reaction mixture.[19] We used a fluorene/endcapper ratio of 18:1 (5.3% endcapper) to obtain a polymer with a M_n of 21 000 g/mol and a polydispersity of 2.1. By comparison, Scherf[19] obtained M_n values of 48 000 ($D = 1.6$) for 4% endcapper and 12 000 ($D = 2.6$) for 9% endcapper. The perylene derivative **13**[20] used maintains the conjugation with the polyfluorene chains, and so, the copolymer **14** exhibits an excellent PL quantum efficiency (>60%) in the solid state. As with the copolymers described previously, energy transfer is not seen in solution but is almost complete in the solid state leading to a narrow red emission with a maximum at 613 nm. Because of their possessing only one or two chromophores in a well-defined spatial relationship, these materials are suitable for studying the process of energy transfer between the chromophores by single molecular spectroscopy techniques. Preliminary investigations[21] have shown that it is possible to distinguish between individual polymer chains bearing one or two chromophores, from which we estimate that approximately 40% of the chains in the sample which bear chromophores bear two dye units, with the remainder having only one chromophore, which is consistent with the observed MALDI-TOF mass spectrum. Studies are also underway into the process of energy transfer between the fluorene and the dye units.

The third type of perylene containing polymer we have synthesized has the perylenes as pendant groups attached to the 9-position of some of the fluorene units. This polymer design has the advantage of permitting the incorporation of a high concentration of perylene dye without affecting the electronic properties of the polyfluorene backbone. The synthesis is shown in Scheme 4. Chloromethylation of a perylene monoimide **15** with chloromethyl methyl ether and tin(IV) chloride at 0 °C proceeded smoothly to give the monochloromethylated derivative **16** (61%). Alkylation of dibromofluorene with 1 equiv each of sterically hindered lithium diisopropylamide (LDA) as base and octyl bromide was found to give an approximately equimolar mixture of starting material and the dioctyl- (**1a**) and monooctylfluorenes, which were separated by column chromatography to give the monooctylfluorene **17** in 24% yield. To account for this product mixture, we postulate that alkylation of the fluorenyl anion and deprotonation of **17** by it to give a monooctylfluorenyl anion, which is then alkylated to give the dioctyl **1a**, occur equally readily. The desired perylene containing monomer **18** was then obtained in 38% yield by alkylation of **17** with **16** using LDA in THF as base. The low yield is due to the alkylating agent **15** undergoing competing side reactions to give a mixture of byproducts, the main component of which was identified by the peak at m/z 988.5 in the mass spectrum as the 1,2-bisperylenylethene **19**, which can be explained as being formed by the deprotonation of **16** followed by alkylation with a second molecule of **16**. Copolymerization of **17** with 2,7-dibromo-9,9-dioctylfluorene **1a** under Yamamoto conditions gave the desired polymer **20**, containing 33 mol % of fluorene units with pendant dyes. Whereas the previous types of polymer with the perylenes attached to the mainchain, either internally or at the ends, show energy transfer only in the solid state, efficient energy transfer to the pendant groups is clearly apparent in the solution PL spectrum of **20** (Figure 8). Even when the excitation is performed at 370 nm (where essentially only the fluorene absorbs), the emission is almost entirely from the perylene. The emission spectra is slightly different in solution and in film. In solution, the emission maximum is at 561 nm

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(20) Schlichting, P.; Duchscherer, B.; Seisenberger, G.; Basche, T.; Bräuchle, C.; Müllen, K. *Chem.—Eur. J.* **1999**, *5*, 2388–2395.

(21) Jäckel, F.; De Feyter, S.; Hofkens, J.; Köhn, F.; Rousseau, E.; De Schryver, F. C.; Ego, C.; Müllen, K., unpublished results.

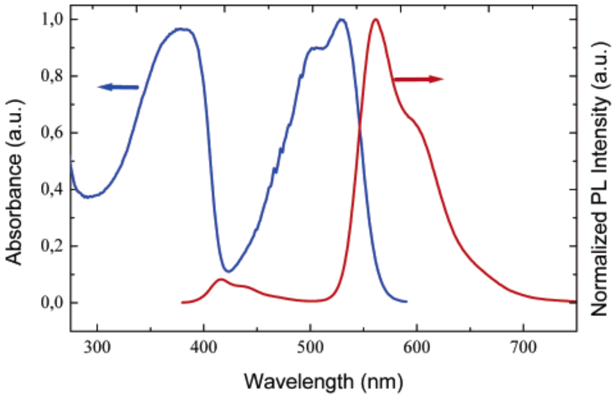

Figure 8. Absorption (blue line) and emission spectra (red line) of copolymer **20** in solution.

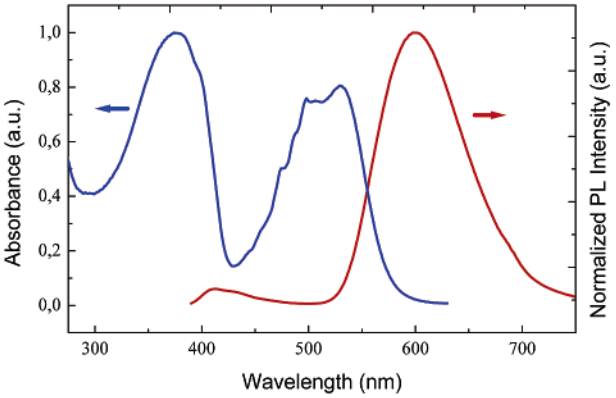

Figure 9. Absorption (blue line) and emission (red line) spectra of a spin-cast film of copolymer **20**.

with a shoulder at 599 nm, while, in the film, the emission maximum is at 599 nm (Figure 9).

That energy transfer can also occur in solution in **20** is unsurprising, given the high concentration of the perylene units in the polymer. This high perylene content also means that there exists a potential percolation pathway for charges to hop from perylene to perylene in the solid state. We have recently shown that perylene dyes make excellent electron acceptors for use in photovoltaic devices.[12] The copolymer **20** is thus a potentially promising candidate for the electron accepting and transporting component in an organic solar cell. A solar cell with an external quantum efficiency of 7% has been made using a blend of **20** and a soluble poly(phenylene vinylene) derivative as an electron donating polymer.[22]

Conclusion

We have synthesized polymers in which perylene dye chromophores are covalently linked to polyfluorenes as statistically distributed comonomers in the polymer backbone, as endcapping units at the chain termini, or as pendant side chains, thus permitting tuning of the emission color through efficient energy transfer to the chromophore units. The statistical copolymers have been used to make efficient LEDs with emission colors covering the whole visible spectra. The end-capped polymers also show color tuning, with control over the molar mass, and are suitable materials for probing the fundamental processes of energy transfer via single molecule spectroscopy. While these two types of polymer show complete energy transfer only in the solid state, the polyfluorene containing perylene as a side chain shows complete energy transfer in solution.

Experimental Section

Thin-film LED structures comprised an O_2 plasma-treated ITO-coated glass anode, a poly(styrene sulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT/PSS) hole injection layer, a poly(fluorene-*co*-perylene) emitter layer, and a Ca−Al cathode. The PEDOT/PSS films (70 nm) were spun from a filtered aqueous solution and then heated to 100 °C under nitrogen for 30 min. The emissive layers (∼100 nm) were spin coated from xylene solutions in a glovebox. The cathode consisting of a 50 nm Ca electron injecting and a 150 nm Al protective layer were deposited in a vacuum ($\sim 5 \times 10^{-6}$ mbar) with patterning by a shadow mask. The EL testing was performed in a vacuum ($\sim 10^{-1}$ mbar) at room temperature under slow-ramped drive conditions.

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Supporting Information Available: Full experimental details for the synthesis of all new materials. Figure illustrating spectral overlap of dyes **2** and **4** with polymer **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0205784

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