Fluorenone-Containing Poly(*p*-phenyleneethynylene)s (PPE) and Poly(fluorenyleneethynylene)s (PFE): Tuning the Solid-State Emission of Alkyne-Bridged Polymers by Interchain Energy Transfer

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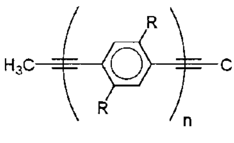
Received July 26, 2001
Revised Manuscript Received September 11, 2001

We report the synthesis of novel poly(*p*-phenyleneethynylene) (PPE, **1**) and poly(fluorenyleneethynylene) (PFE, **2**) derivatives, **3** and **4**, that contain fluorenone units as active lumophores. The solution and solid-state absorption and emission properties of these materials are reported. Acyclic diyne metathesis (ADIMET) is a powerful method to prepare alkyne-bridged polymers such as PPE and PFE.[1] While the PPEs show exciting optical properties,[1f] they are only weakly greenish-yellow fluorescent in the solid state, a testimony to aggregate formation and concomitant Davydov split of the excited state,[2] while the PFEs are strongly blue solid-state emitting.[1] Their ease of synthesis, high molecular weight, stability, and purity makes both PPEs and PFEs attractive as materials in organic semiconductor-type applications such as PLEDs.[1,3] It would be of fundamental and practical importance to tune their emission over the whole spectral range. In inorganic semiconductors, this color tuning is achieved by doping the matrix with p- or n-type materials,[4] creating electronic states that reduce the band gap. In organic polymers, this type of covalent "doping" has been less popular, despite the important work done in the groups of Müllen[5−7] and Miller.[8] They covalently introduced emitter molecules (anthracene, perylene, pyrene) into the backbones of several different conjugated polymers, including dialkylpolyfluorene and dialkoxy−PPE.[9] In these systems, solid-state emission arises from exciton migration to local minima from which emission occurs.



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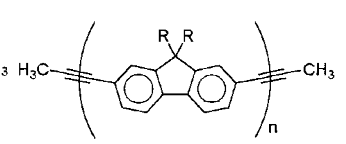

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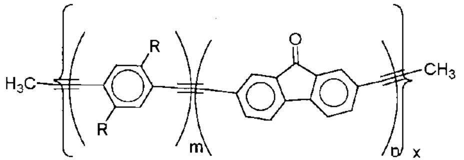

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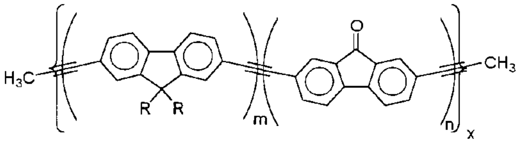

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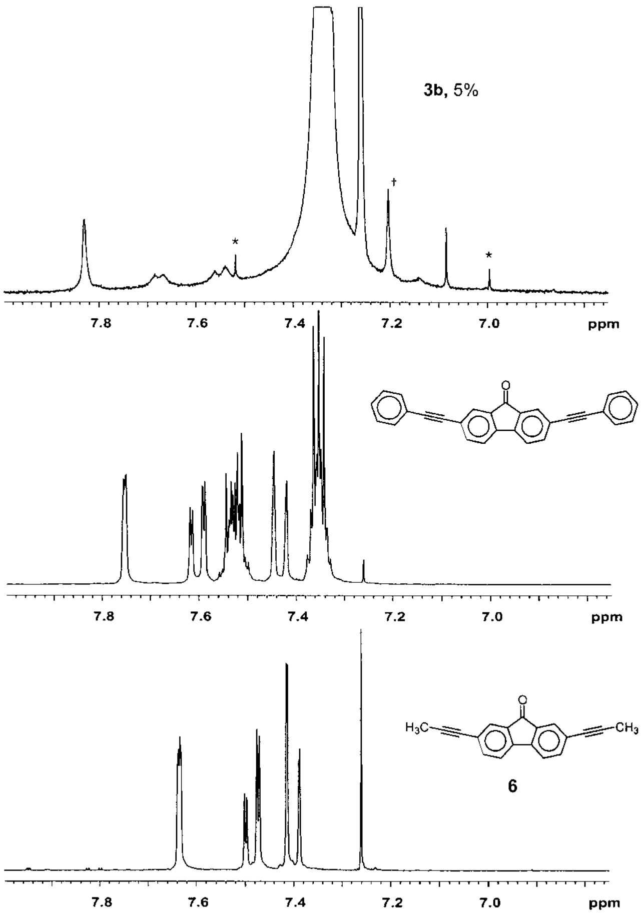

Figure 1. Comparison of the ^{1}H NMR spectra of **3b** (5%); 2,7-bis(phenylethynyl)fluorene, and **6**. The stars in the spectrum of **3b** represent the ^{13}C satellites of CDCl$_3$; the band at 7.20 ppm (†) is a spinning sideband of CHCl$_3$. The band at 7.08 ppm is attributed to an end group signal.

ADIMET of **5a**,**b** in the presence of 2−10% **6**[10] furnishes the copolymers **3a**,**b**[11] in yields ranging from 75 to 93% as bright orangish-yellow, well-soluble, film-forming powders. In the same way, 10% of **6** and 90% of monomer **7** gave the copolymer **4**.[12] Fortuitiously, **6** is incorporated into the polymer chains of PPE and PFE, and the catalytic system is not disturbed by the keto groups in **6**. The incorporation of the fluorenone residues into the polymers is evidenced by IR ($\nu = 1723$ cm^{-1}) and fluorescence spectroscopies (vide infra). For copolymers **3** with a content of $\geq 2\%$ fluorenone (see ref 13) ^{1}H NMR spectroscopy displays low-field shifted signals (δ 7.83, 7.69, 7.55) that must be attributed to the fluorenone core. The signals appear at lower field than those of **6**[10] and even than those of 2,7-bis(phenylethynyl)fluorenone (Figure 1). These experiments exclude the isolated materials to be physical mixtures of **6** and **1** or of **6** and **2**.

Copolymer **4** shows the most interesting optical properties. In solution the absorption and emission spectra are identical to those of **2** (Table 1) and in the solid state, the absorption spectra of **2** and **4** in thin films are very similar. However, their solid-state emission spectra are *very* different (Figure 2). In thin films of **2**, blue emission is observed,[1e] while in films of **4** only *an orange emission centered at 533 nm is recorded*. All

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10.1021/ma011330m CCC: $20.00

Scheme 1

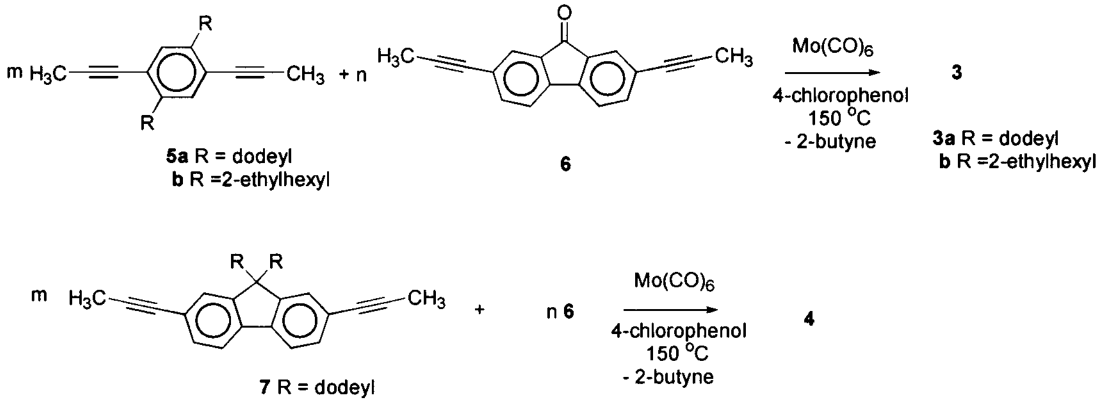

Table 1. Yields, GPC Data, and Optical Characterization of Polymers 3 and 4

polymer; % **6**	substituent R	GPC yield (%)	GPC P_n[a]	GPC M_w/M_n	absorption solution	absorption thin film	emission solution	emission thin film (annealed)
3a; 2%	dodecyl	81	195	4.2	398	437	426, 450	539 (533)
3a; 5%	dodecyl	83	49	2.3	386	436	425, 447	534 (531)
3a; 10%	dodecyl	75	143	8.8	392	439	429, 450	544 (537)
3b; 5%	ethylhexyl	93	202	11.0	388	430	425, 450	522 (523)
4a; 10%	dodecyl	90	48	3.5	388, 406	416	428, 447	531 (533)
1a[b]	dodecyl		89	4.7	384	413, 440	426, 445	534 (452, 487, 502, 528 (sh))
1b[b]	ethylhexyl		119	3.2	384	400, 438	431, 451	441, 466, 487 (442, 468, 488)
2[c]	dodecyl		98	4.4	388, 407	392, 418	428, 454	429, 454 (−)

[a] P_n are repeat units based upon polystyrene standard. [b] According to Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605. [c] Pschirer, N. G.; Bunz, U. H. F. *Macromolecules* **2000**, *33*, 3961.

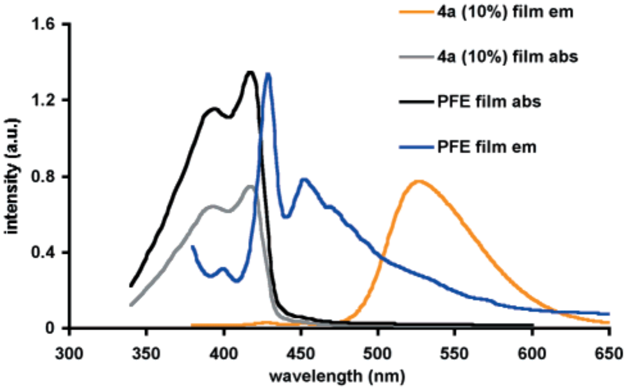

Figure 2. Thin film absorption and emission ($\lambda_{exc} = 390$ nm) spectra of **2** and **4** (10% fluorenone content). In **2** the Stokes shift is very small, while thin films of **4** only show fluorenone-centered, bright emission with a very large stokes shift. The main emission of **4** is at λ_{max} of 540 nm, i.e., 110 nm red-shifted from the emission of **2**.

emission from the PFE skeleton is suppressed. Efficient energy transfer from the PFE-part to the fluorenone takes place in the solid state but not in solution, where exciton migration along the polymer backbone is not very efficient. Rotational decoupling or coiling of the polymer chain may be the explanation. It is interesting to note that Miller's copolymers show both emission from the polyfluorene and from the perylene in solution. This may be a combined result of perylene's highly emissive nature and the higher doping concentration in their copolymers (15%). We observe *only* blue emission from the PFE or PPE backbone in solution (some fluorenone emission is observed for copolymers with >25% fluorenone content), while only orangish-yellow, fluorenone-centered emission is observed in thin films. In the solid state planarization of the polymer backbone almost certainly enhances conjugation of the fluorenone and the PFE parts, while the lamellar order places the fluorenone lumophores into close spatial contact to several polymer chains. Intra- and intermolecular (Förster) energy transfer are effective to funnel the excitation energy into the LUMO of fluorenone from which efficient orangish-yellow emission takes place (see Figure 2). Physical mixtures of PFE with dipropynylfluorenone **6** do not show this behavior.

In that regard, copolymers **3** are similar to **4**. PPEs **1** show blue-shifted solid-state emission upon annealing in the solid state. In pristine samples of the copolymers **3**, the emission of the fluorenone-containing lumophore is detected, resulting in emission which is both red-shifted and strongly intensified with respect to the greenish solid-state emission of didodecyl-PPE. Upon annealing resulting in increased ordering of the samples,[13] the thin film emission spectra do not change, suggesting an effective inter/intramolecular energy transfer from the PPE-backbone to the fluorenone similar as to discussed in the PFE-hybrids **4**. The absence of observable excimer emission seems to be a result of the reduced amount of active lumophores,[8] which are unaffected by polymer alignment. This effect is observed in PPEs at fluorenone contents > 2% weight of monomer feed.

In conclusion, we have demonstrated that covalent doping of PPE and PFE with fluorenone utilizing alkyne metathesis is feasible. While doping levels of 2−10% show no effect on *solution* emission, they are sufficient to ensure complete energy transfer into the dopant sites and lead to efficient *orange solid-state* emission of these interesting conjugated polymers. *Intra*- and *inter*-chain energy transfer is the cause of such behavior. In future, we will report upon the introduction of other highly fluorescent dopants into PPE-types. An added-on appealing feature of the ketone-containing polymers **3** and **4** is their principal usefulness in postfunctionalization schemes (see Scheme 1), in which the C═O double bond could be converted into a host of other functionalities.

Acknowledgment. We thank Perry Pellechia for his help with the ^{1}H NMR plots and the Petroleum Research Funds for generous funding. U.H.F.B. is Camille Drefus Teacher-Scholar (2000−2004). N.G.P. thanks the College of Science and Mathematics of the University of South Carolina for a Graduate School Dissertation Fellowship, and K.B. is an NSF REU participant.

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(10) **Synthesis of 6.** CrO_3 24.0 g (240 mmol) and diiodofluorene (41.8 g, 100 mmol) in acetic anhydride (600 mL) were stirred at room temperature for 12 h. The reaction mixture was poured into 500 mL of a 2% HCl solution, filtered, and recrystallized from 2-propanol to isolate diiodoflurenone (36.2 g, 84%). To a 1 L Schlenk flask, flushed with N_2, was added diiodofluorenone (9.10 g, 21.1 mmol), $Pd(PPh_3)_2Cl_2$ (200 mg, 0.208 mmol), CuI (100 mg, 0.631 mmol), and piperidine (70 mL). The flask was evacuated, filled with propyne gas, and shaken for 16 h. Filtration over Celite (2:1 hexanes/CH_2Cl_2) and crystallization from EtOH furnishes **6** (3.94 g, 73%). Mp: 127−129. ^{1}H NMR ($CDCl_3$): δ 7.60 (d, $J = 0.8$, 2H), 7.46 (dd, $J = 7.0$, 1.7 Hz, 2H), 7.37 (dd, $J =$ 7.7,0.8 Hz, 2H), 2.04 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 141.9, 132.5, 122.8, 93.1, 34.2, 32.0, 30.8, 29.8, 29.7, 29.4, 22.7, 14.1. IR (neat): ν (cm^{-1}) 2954, 2920, 2850, 1723, 1503, 1467, 1093, 885, 720.

(11) **Synthesis of 3.** Dipropynyls **5a**,**b** or **7** and **6**, $Mo(CO)_6$ (5 mol %), and 4-chlorophenol (1 equiv with respect to **5** or **7**) are dissolved in 1,2-dichlorobenzene (10−15 mL for 1−2 g of monomer) and heated to 150 °C for 24 h under a steady stream of N_2. To the resulting solution was added 50 mL of $CHCl_3$. The organic portion was washed with 10% NaOH, 10% HCl, and H_2O and then poured into 400 mL MeOH for precipitation. **3a** (2%). ^{1}H NMR ($CDCl_3$): δ 7.81 (s), 7.67−7.63 (m), 7.59−7.52 (m), 7.36 (bs), 7.29 (s), 7.12−7.11 (m), 7.07−7.05 (m), 6.98 (s), 2.81 (bs), 2.05 (s), 1.70 (bs), 1.52 (s), 1.51−1.23 (m), 0.85 (t, $J = 7.1$). ^{13}C NMR ($CDCl_3$): δ 141.9, 132.5, 122.8, 93.1, 34.2, 32.0, 30.8, 29.8, 29.7, 29.4, 22.7, 14.1. IR (neat): ν (cm^{-1}) 2954, 2920, 2850, 1723, 1503, 1467, 1093, 885, 720. **3a** (5%). ^{1}H NMR ($CDCl_3$): δ 7.81 (bs), 7.67−7.63 (m), 7.54−7.52 (m), 7.36 (bs), 7.35 (s), 7.34 (s), 7.29 (s), 7.22 (s), 2.82 (bm), 2.70 (m), 2.10 (s), 1.70 (m), 1.61 (s), 1.53−1.23 (m), 0.85 (t). ^{13}C NMR ($CDCl_3$):δ 141.9, 141.7, 134.5, 132.4, 123.4, 122.8, 121.9, 93.1, 92.5, 91.3, 90.3, 77.2, 34.2, 33.9, 32.0, 30.8, 30.5, 29.8, 29.7, 29.5, 29.4, 22.7, 14.2, 4.6. IR (neat): ν (cm^{-1}) 2955, 2920, 2850, 1723, 1502, 1466, 892, 720. **3a** (10%). ^{1}H NMR ($CDCl_3$): δ 7.80 (s), 7.65−7.60 (m), 7.59−7.56 (m), 7.36 (bs), 6.98 (s), 2.81 (bm), 2.10 (s), 1.70 (bm), 1.52 (bs), 1.51−1.23 (m), 0.85 (bs). ^{13}C NMR ($CDCl_3$): δ 141.9, 132.4, 122.8, 93.1, 34.2, 31.9, 39.8, 29.8, 29.7, 29.4, 22.7, 14.1. IR (neat): ν (cm^{-1}) 2920, 2850, 1723, 1503, 1466, 856. **3b** (5%). ^{1}H NMR ($CDCl_3$): δ 7.83 (s), 7.69 (bd), 7.55 (bd), 7.36 (s), 7.35−7.34 (m), 7.29 (s), 7.22 (s), 2.82 (bm), 2.70 (m), 2.10 (s), 1.70 (m), 1.61 (s), 1.53−1.23 (m), 0.85 (t). ^{13}C NMR ($CDCl_3$): δ 141.0, 133.4, 123.1, 93.3, 77.4, 40.3, 38.5, 32.5, 28.8, 25.6, 23.1, 14.1, 10.8. IR (neat): ν (cm^{-1}) 2955, 2920, 2850, 1738, 1461, 1376, 1238, 1019, 904.

(12) **4** (10%). ^{1}H NMR ($CDCl_3$): δ 7.86 (d, $J = 13.6$ Hz), 7.71−7.66 (m), 7.65 (s), 7.64−7.50 (m), 7.46, (d, $J = 7.7$ Hz), 7.47−7.34 (m), 2.09 (s), 2.07 9s), 1.99 (bm), 1.19−1.04 (bm), 0.85−0.81 (m), 0.59 (bm). ^{13}C NMR ($CDCl_3$): δ 151.1, 151.0, 140.7, 140.0, 130.8, 130.5, 125.9, 122.7, 122.0, 121.7, 120.0, 119.9, 90.8, 90.7, 86.1, 80.6, 55.3, 40.5, 31.9, 30.1, 29.6, 29.4, 29.3, 23.8, 22.7, 14.1, 4.5. IR (neat): ν (cm^{-1}) 2954, 2916, 2852, 1726, 1464, 1126, 885, 823.

(13) Integration of the ^{1}H NMR aromatic signals suggests a lower incorporation of fluorenone units by a factor of 0.5 when compared to monomer addition (**6**), i.e., **3a** 5% contains roughly 2.5% fluorenone.

(14) Thin films were heated past their isotropic point as determined by DSC, cooled to their LC phase, and left at this teperature for 2 h, then slowly cooled to ambient temperature. An increase in chain ordering was evidenced by powder XRD.

MA011330M