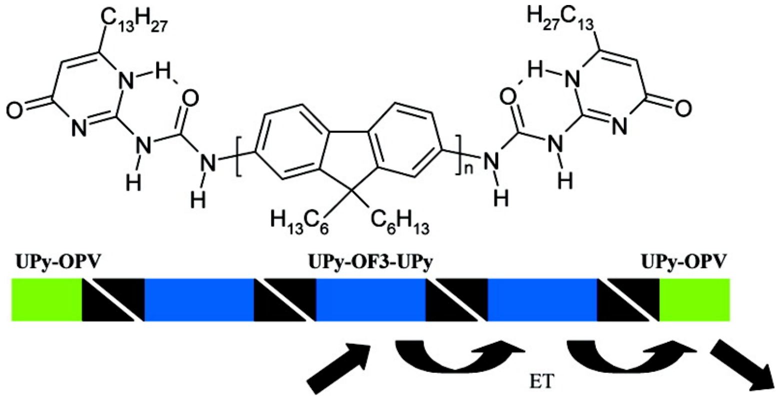
Article

Synthesis and Energy-Transfer Properties of Hydrogen-Bonded Oligofluorenes

Stephen P. Dudek, Maarten Pouderoijen, Robert Abbel, Albertus P. H. J. Schenning, and E. W. Meijer

J. Am. Chem. Soc., **2005**, 127 (33), 11763-11768• DOI: 10.1021/ja052054k • Publication Date (Web): 29 July 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
ARTICLES

Synthesis and Energy-Transfer Properties of Hydrogen-Bonded Oligofluorenes

Stephen P. Dudek, Maarten Pouderoijen, Robert Abbel,
Albertus P. H. J. Schenning,* and E. W. Meijer*

Contribution from the Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Received March 31, 2005; E-mail: a.p.h.j.schenning@tue.nl; e.w.meijer@tue.nl

---

Abstract: A set of fluorene oligomers has been synthesized by stepwise palladium-catalyzed (Suzuki) couplings of fluorene monomers. Ureidopyrimidinones (UPy), functional groups that can dimerize via quadruple hydrogen bonds, were attached to both ends of the oligofluorenes. The resulting bis-UPy-terminated oligomers self-assemble into supramolecular chain polymers. For comparison, oligofluorenes of the same oligomer lengths but without terminal hydrogen-bonding groups were synthesized. Chains of hydrogen-bonded fluorenes can be simply endcapped by a variety of chain stoppers, molecules that have one UPy group. In this manner, we have endcapped the hydrogen-bonded fluorene chains with either oligo(*p*-phenylenevinylene) or perylene bisimide. Energy-transfer experiments in solution and the solid state demonstrate that oligofluorenes can donate energy to a variety of energy acceptors, but that this energy transfer occurs most effectively when the donor fluorene is hydrogen-bonded to the acceptor.

Introduction

π-Conjugated polymers[1] have been extensively investigated as alternatives to inorganic semiconductor components in devices such as field-effect transistors, solar cells, and light-emitting diodes. Polymers, however, can suffer from inhomogeneities such as chain defects that may limit electronic performance. Instead, many groups[2,3] have synthesized and studied defect-free π-conjugated oligomers to determine how the electronic properties of a material change with chain length.[3,4] Yet, it can be difficult to synthesize oligomers that are long enough to have mechanical properties useful for incorporation into devices. Short oligomers often need to be vacuum-deposited and do not readily form films.

The well-defined electronic properties of the monodisperse oligomer and the processability of a polymer can be combined using supramolecular polymers composed of oligomers. Previously, we attached a conjugated oligo(*p*-phenylenevinylene) to aliphatic molecules bis-terminated with self-complementary hydrogen-bonding groups,[5] resulting in supramolecular hydrogen-bonded polymers useful in photovoltaic devices.[6] One advantage of supramolecular polymers is their modularity, permitting tuning of the polymer's electronic properties. For example, the emission wavelength in supramolecular polymers can be adjusted by mixing in other emissive units functionalized with hydrogen-bonding groups without having phase segregation between the energy donor and acceptor material. To demonstrate this concept of modularity, we have chosen to work with oligomers of fluorene (Chart 1). Chiefly explored for blue light-emitting diodes, oligo- and polyfluorenes[7] are thermally stable and have high fluorescence quantum yields.[8−13] 2-Ureido-4[1*H*]-pyrimidinone (UPy)[14] groups were attached to the ends of a set of oligofluorenes (Chart 1, UPy-OF*n*-UPy). The UPy group dimerizes strongly via four hydrogen bonds with a dimerization constant of 6×10^{-7} M in chloroform[15] (Chart 1). The blue emissive bis-UPy oligofluorenes can be endcapped with either UPy-terminated oligo(*p*-phenylenevinylene) or perylene bisimide, green and red emissive dyes, respectively (Chart 1).

---

[1] Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* **1992**, *357*, 477−479.

[2] Maddux, T.; Li, W. J.; Yu, L. P. *J. Am. Chem. Soc.* **1997**, *119*, 844−845.

[3] Meier, H.; Stalmach, U.; Kolshorn, H. *Acta Polym.* **1997**, *48*, 379−384.

[4] Klaerner, G.; Miller, R. D. *Macromolecules* **1998**, *31*, 2007−2009.

[5] Folmer, B. J. B.; Sijbesma, R. P.; Versteegen, R. M.; van der Rijt, J. A. J.; Meijer, E. W. *Adv. Mater.* **2000**, *12*, 874−878.

[6] El-ghayoury, A.; Schenning, A. P. H. J.; van Hal, P. A.; van Duren, J. K. J.; Janssen, R. A. J.; Meijer, E. W. *Angew. Chem., Int. Ed.* **2001**, *40*, 3660−3663.

[7] (a) Fukuda, M.; Sawada, K.; Yoshino, K. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 2465. (b) Bernius, M. T.; Inbasekaran, M.; O'Brien, J.; Wu, W. S. *Adv. Mater.* **2000**, *12*, 1737−1750. (c) Ranger, M.; Leclerc, M. *Macromolecules* **1997**, *30*, 7686−7691.

[8] Liu, B.; Wang, S.; Bazan, G. C.; Mikhailovsky, A. *J. Am. Chem. Soc.* **2003**, *125*, 13306−13307.

[9] Jo, J.; Chi, C.; Höger, S.; Wegner, G.; Yoon, D. Y. *Chem.−Eur. J.* **2004**, *10*, 2681−2688.

[10] Lee, S. H.; Tsutsui, T. *Thin Solid Films* **2000**, *363*, 76−80.

[11] Anémian, R.; Mulatier, J.-C.; Andraud, C.; Stéphan, O.; Vial, J.-C. *Chem. Commun.* **2002**, 1608−1609.

[12] (a) Geng, Y.; Trajkovska, A.; Katsis, D.; Ou, J. J.; Culligan, S. W.; Chen, S. H. *J. Am. Chem. Soc.* **2002**, *124*, 8337−8347. (b) Katsis, D.; Geng, Y. H.; Ou, J. J.; Culligan, S. W.; Trajkovska, A.; Chen, S. H.; Rothberg, L. J. *Chem. Mater.* **2002**, *14*, 1332−1339. (c) Geng, Y.; Culligan, S. W.; Trajkovska, A.; Wallace, J. U.; Chen, S. H. *Chem. Mater.* **2003**, *15*, 542−549.

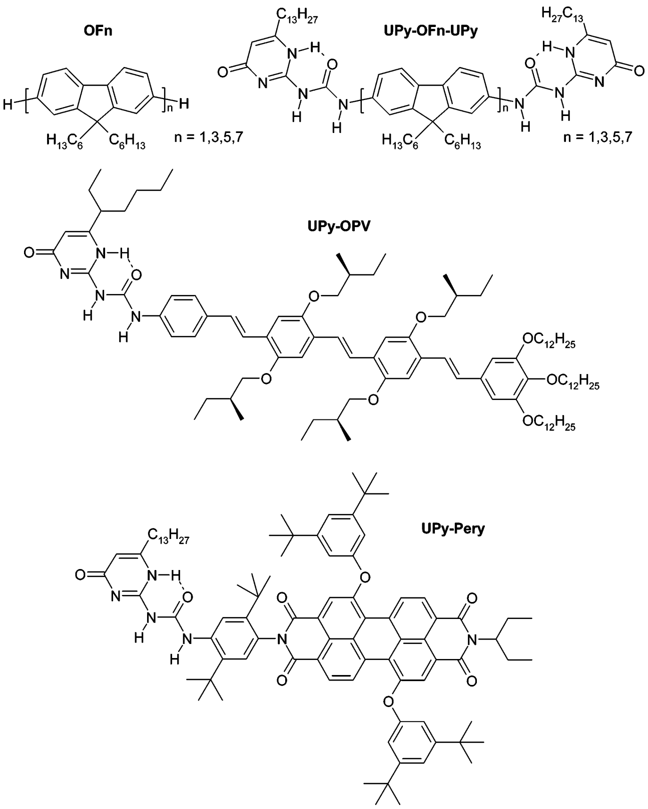
[13] (a) Jäckel, F.; De Feyter, S.; Hofkens, J.; Köhn, F.; De Schryver, F. C.; Ego, C.; Grimsdale, A.; Müllen, K. *Chem. Phys. Lett.* **2002**, *362*, 534−540. (b) Ego, C.; Marsitzky, D.; Becker, S.; Zhang, J.; Grimsdale, A. C.; Müllen, K.; MacKenzie, J. D.; Silva, C.; Friend, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 437−443. (c) Kong, X.; Jenekhe, S. A. *Macromolecules* **2004**, *37*, 8180−8183.

[14] Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Hirschberg, J. H. K. K.; Lange, R. F. M.; Lowe, J. K. L.; Meijer, E. W. *Science* **1997**, *278*, 1601−1604.

[15] Söntjens, S. H. M.; Sijbesma, R. P.; van Genderen, M. H. P.; Meijer, E. W. *J. Am. Chem. Soc.* **2000**, *122*, 7487−7493.

10.1021/ja052054k CCC: $30.25 © 2005 American Chemical Society

Chart 1. Chemical Structure of the Synthesized Oligofluorenes (**OF*n***), Bis-UPy-Terminated Oligofluorenes (**UPy-OF*n*-UPy**), UPy-Terminated Oligo(*p*-phenylenevinylene) (**UPy-OPV**), and UPy-Terminated Perylene Bismide (**UPy-Pery**)



Energy-transfer experiments demonstrate that these oligofluorenes can efficiently donate energy to both energy acceptors. Previously, we reported energy donor−acceptor systems connected by (uriedo)triazine hydrogen bonds.[16,17] However, this hydrogen-bonded system required additional π-stacking between the donor and acceptor groups for room temperature stability. The dimerization constant of the UPy groups is more than 100 times stronger than that for uriedotriazine systems, permitting polymer assemblies based purely on hydrogen bonding.

Results and Discussion

Synthesis. The synthesis of simple, nonterminated oligofluorenes has been reported by several research groups,[9] most notably Tsutsui,[10] Vial,[11] and Chen.[12] A similar synthetic strategy was adopted here to construct the fluorene backbone of both the hydrogen- and UPy-terminated oligofluorenes (**OF*n***, **UPy-OF*n*-Upy**, Chart 1, Schemes 1 and 2). The fluorene chain was elongated by stepwise Pd(0) (Suzuki) coupling of two asymmetric fluorene monomers to both ends of a symmetric bis-functionalized mono- or oligofluorene core. The trimethylsilyl (TMS) group serves as a halogen-protecting group: the trimethylsilyl group can be first introduced through lithiation of a bromofluorene followed by addition of trimethylsilyl chloride; the TMS group is tolerant of the pursuant Suzuki coupling, after which it can be converted back to a halogen with iodo monochloride. To expedite the synthesis of longer oligomers, asymmetric fluorene dimers were synthesized. Fluorene dimers **7** and **12** are generated along with symmetric fluorene trimers from Suzuki couplings (Scheme 1); the asymmetric dimers can be readily separated from the symmetric trimers by silica gel column chromatography. Coupling of dimer fragments instead of monomer fragments to both ends of the fluorene core reduces the number of coupling steps required to make longer oligomers.

Bis-UPy-oligofluorenes were synthesized by attachment of activated ureidopyrimidinones to bis-NH_2-terminated oligofluorenes (Scheme 2). Since the palladium-catalyzed coupling of fluorenes did not proceed in the presence of either the UPy or NH_2 functional group under standard Suzuki conditions, an amine-protecting group was sought. Although there are several ways to introduce amine functionality on fluorenes, nitration[18] of a fluorene monomer followed by reduction of the nitro group after the oligofluorene chain is constructed was chosen as the most robust and simplest method.[19] Nitration of oligofluorenes longer than one unit generated products that were multiply nitrated along the chain and not just at the desired terminal positions. Therefore, first a fluorene monomer building block was singly nitrated (**14**), next the nitro monomer was incorporated into the oligofluorene chain by Suzuki coupling, and finally the bis-nitro-oligofluorene was reduced to the bis-amine counterpart as a penultimate step. Reduction of the bis-nitro-fluorene monomer and trimer proceeded smoothly by hydrogenation on palladium/carbon, but this method was too sluggish for the longer oligomers. For the pentamer and heptamer, $SnCl_2$ reduction proved more effective. One main advantage of this stepwise conversion of bis-nitro-terminated oligofluorenes to bis-amines and then to bis-ureidopyrimidinones is the successive change in polarity of the products after each transformation. The increase in polarity easily permits separation by column chromatography of the desired products from undesired non- or singly functionalized oligomers.

The syntheses of the hydrogen-bonded oligophenylenevinylene (**UPy-OPV**, Chart 1) and perylene bisimide acceptors (**UPy-Pery**, Chart 1) are based on previously reported synthetic routes (Scheme 3).

The **OF*n*** and **UPy-OF*n*-UPy** and intermediate products were characterized by standard techniques such as ^{1}H NMR, ^{13}C NMR, MALDI-TOF, IR, and elemental analysis (see Supporting Information). The hydrogen-terminated oligofluorenes are flocculent white powders; the bis-UPy-terminated oligofluorenes consist of pale brown thin films suggesting substantial intermolecular hydrogen bonding. Likewise, the **OF*n*** is sufficiently soluble in common organic solvents such as THF or $CHCl_3$, while the **UPy-OF*n*-UPy** has low solubility in these solvents. The solubility of **UPy-OF*n*-UPy** in chloroform increases with chain length. On addition of a small amount of a competing hydrogen bond source such as trifluoroacetic acid (TFA) or

---

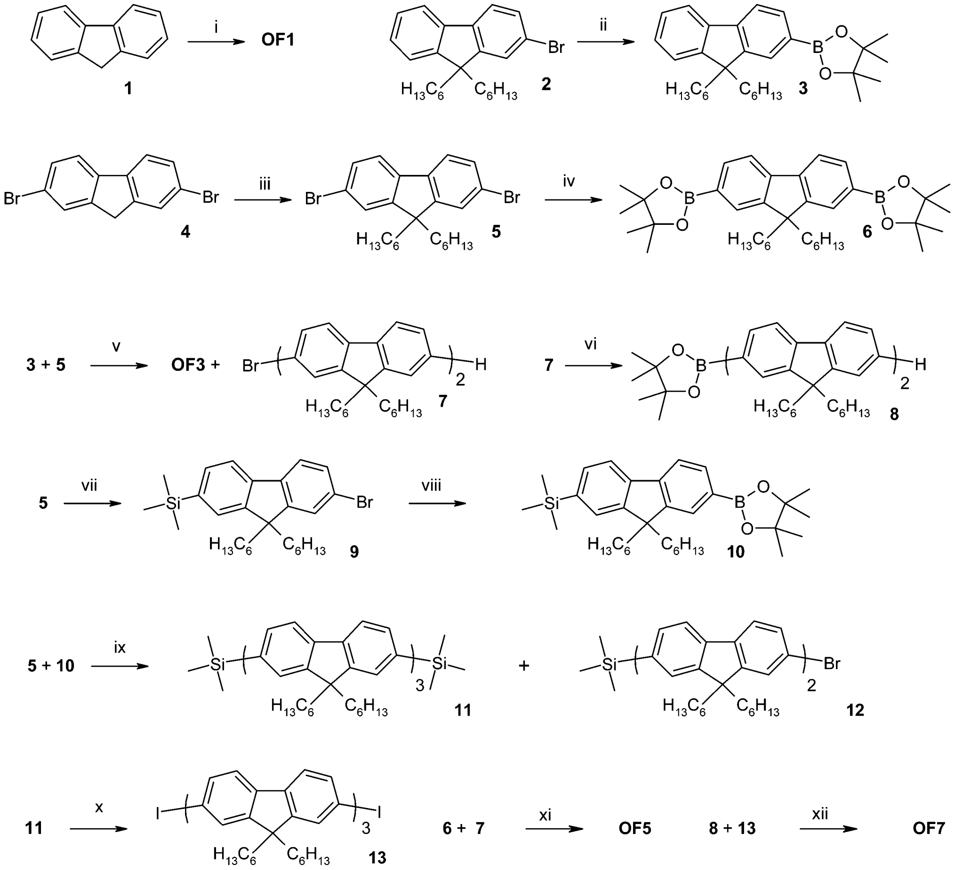
(16) Hoeben, F. J. M.; Herz, L. M.; Daniel, C.; Jonkheijm, P.; Schenning, A. P. H. J.; Silva, C.; Meskers, S. C. J.; Beljonnne, D.; Phillips, R. T.; Friend, R. H.; Meijer, E. W. *Angew. Chem., Int. Ed.* **2004**, *43*, 1976−1979.

(17) Schenning, A. P. H. J.; van Herrikhuijzen, J.; Jonkheijm, P.; Chen, Z.; Wurthner, F.; Meijer, E. W. *J. Am. Chem. Soc.* **2002**, *124*, 10252−10253.

(18) Halles, G.; Hepworth, J. D.; Waring, D. R. *J. Chem. Soc. B* **1970**, 975−979.

(19) Incorporation of amine functionality was also attempted via attachment of phthalimide (Gabriel reaction) to bromofluorenes followed by hydrazine cleavage of the phthalimide, but this route led to lower yields and incomplete cleavage of the phthalimide. See: (a) Sato, M.; Ebine, S.; Akabori, S. *Synthesis* **1981**, 472−473. (b) Grisorio, R.; Mastrolilli, P.; Nobile, C. F.; Romanazzi, G.; Suranna, G. P.; Meijer, E. W. *Tetrahedron Lett.* **2004**, *45*, 5367−5370.

Scheme 1. Synthesis of **OF*n***[a]



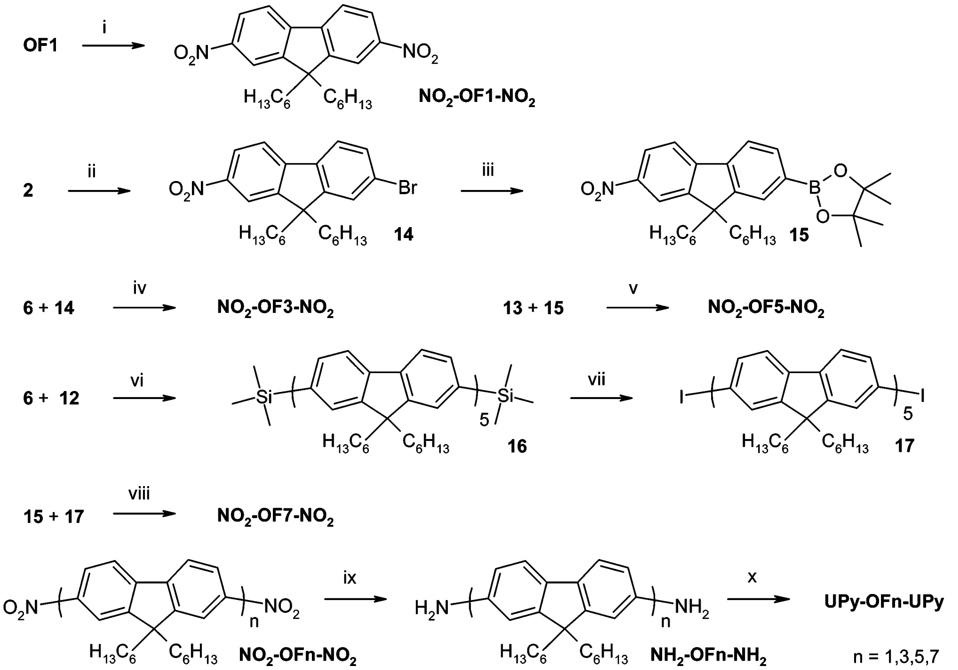
[a] Reaction conditions: (i, iii) $C_6H_{13}Br$, DMSO/aq NaOH, 96% (**OF1**), 46% (**5**); (ii, iv, vi, viii) *n*BuLi, 2-isopropoxy-pinacolatoborolane, THF, −78 °C, 98% (**3**), 77% (**6**), 72% (**8**), 45% (**10**); (v, ix, xi, xii) $Pd(PPh_3)_4$, Na_2CO_3, dioxane, 90 °C, 54% (**OF3**) and 39% (**7**), 73% (**11**) and 27% (**12**); 74% (**OF5**), 46% (**OF7**); (vii) *n*BuLi, TMSCl, Et_2O, −78 °C, 81% (**9**); (x) ICl, CH_2Cl_2, 4 °C, 86%.

hexafluoro-2-propanol, the bis-UPy-terminated oligofluorenes do dissolve readily in common organic solvents. The ^1H NMR spectra of the **UPy-OF*n*-UPy** show that the ureidopyrimidinone protons are shifted strongly downfield to 12.3, 12.4, and 13.1 ppm, indicating hydrogen bonding.[14] On addition of TFA, the three downfield signals disappear (see Supporting Information). No enol tautomeric proton signals are present in the NMR spectrum, suggesting that the pyrimidinones are predominately in the keto tautomer. When **UPy-OF*n*-UPy** solutions are serially diluted, the ^1H NMR peak positions of the pyrimidinone protons do not shift and no cyclic structures are observed. Assuming an association constant similar to earlier reported UPy systems,[15] the virtual degree of polymerization is about 10 000 at a concentration of 1 M.

Optical Properties. Figure 1a shows the UV−visible spectra of the bis-UPy-terminated oligofluorene series as compared with the spectra of the parent hydrogen-terminated oligofluorenes. All samples were dissolved in chloroform at a constant concentration of 6×10^{-7} M. Both sets of oligofluorenes, UPy- and hydrogen-terminated, absorb strongly between 325 and 425 nm with vibronically unstructured bands. The hydrogen-terminated monomer, **OF1**, has a much lower absorption due to its short conjugation length. The peak position of maximum absorption (λ_{max}) shifts bathochromically with increasing oligomer length; likewise, the extinction coefficient increases with oligomer length. These trends are similar to those reported for oligofluorenes[4,9,10] and other sets of π-conjugated oligomers.[3] The bis-UPy-terminated oligofluorenes absorb more strongly than their hydrogen-terminated oligofluorene counterparts. This slight increase in the extinction coefficient for the bis-UPy oligofluorenes may be due to electron donation by the urea groups, enlarging the effective conjugation length of the oligofluorene to which it is attached. Table 1 summarizes absorption and photoluminescence spectra for oligofluorenes in $CHCl_3$.

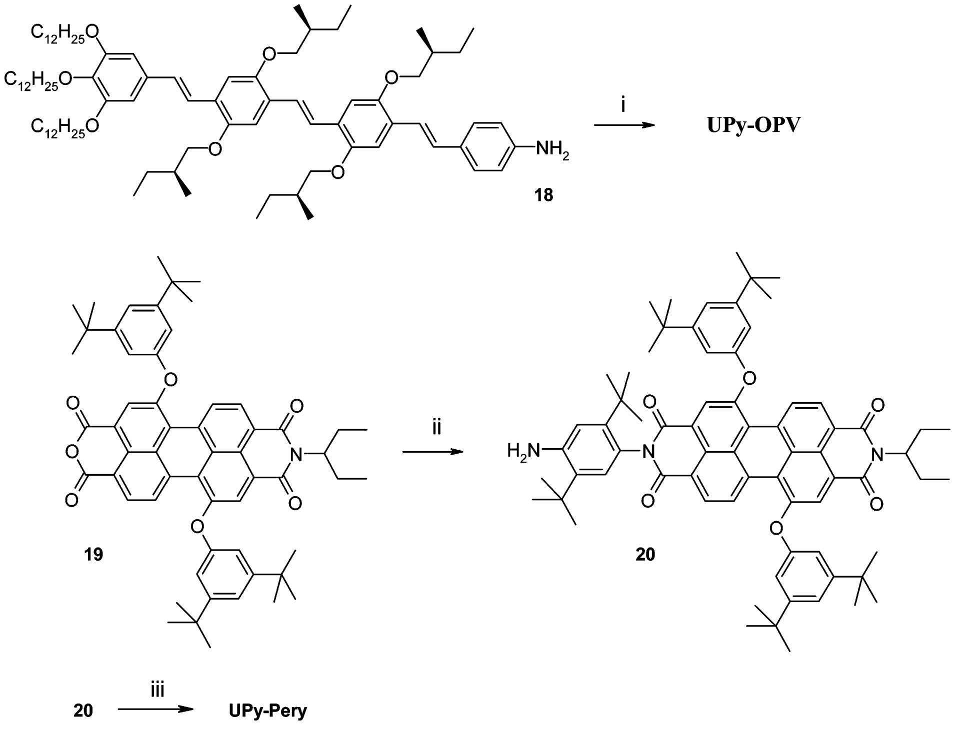
When excited at their respective maximum absorption wavelengths, the oligofluorenes emit strongly. The fluorescence spectra of these compounds show three primary vibronically structured bands with vibronic spacing of about 1300 cm^{-1}. As with absorption, the fluorescence spectra exhibit a bathochromic shift with increasing oligomer length (Figure 1b). The bis-UPy-terminated oligo-9,9-dihexylfluorene series appears to have a maximum fluorescence effective conjugation length of about five units as the fluorescence peak maximum does not shift appreciably further with increasing chain length. For comparison, Klaerner and Miller[4] report a fluorescence effective conjugation length of six fluorene units for oligo-9,9-dihexylfluorene. The bis-UPy-terminated oligofluorenes fluoresce less strongly than the hydrogen-terminated oligofluorenes of the same length. The fluorescence quantum yields (Φ_{PL}) of the fluorenes were determined relative to that of quinine sulfate and anthracene (Table 1).[20] Except for the monomer, the nonterminated oligofluorenes **OF*n*** have high quantum yields (0.88−0.96) that are approximately the same. The trimer **OF3**

Scheme 2. Synthesis of **UPy-OF*n*-UPy**[a]



[a] Reaction conditions: (i, ii) HNO_3/HOAc, 53% (**NO_2-OF1-NO_2**), 98% (**14**); (iii) bis(pinacolato)diboron (Bpin), Pd(dppf)Cl_2, NaOAc, DMF, 90 °C, 52%; (iv, v, vi, viii) $Pd(PPh_3)_4$, Na_2CO_3, dioxane, 90 °C; 97% (**NO_2-OF3-NO_2**), 68% (**NO_2-OF5-NO_2**), 68% (**16**), 83% (**NO_2-OF7-NO_2**); (vii) ICl, CH_2Cl_2, 4 °C, 100%; (ix) H_2, Pd/C, MeOH/CH_2Cl_2, or $SnCl_2$, EtOH/EtOAc, reflux 19−74%; (x) *N*-(6-tridecyl-4[1*H*]-pyrimidinon-2-yl)-1*H*-imidazole-1-carboxamide, $CHCl_3$, 64−100%.

Scheme 3. Synthesis of **UPy-OPV** and **UPy-Pery**[a]



[a] (i) UPy-imidazolide, $CHCl_3$, reflux, 85%; (ii) 1,4-diamino-2,5-di-t-butylbenzene, $Zn(OAc)_2$, DMA, reflux, 80%; (iii) *N*-(6-tridecyl-4[1*H*]-pyrimidinon-2-yl)-1*H*-imidazole-1-carboxamide, $CHCl_3$, reflux, 67%.

has the highest Φ_{PL} of the **OF*n*** series. The bis-UPy-terminated oligofluorene series exhibits stronger variation of Φ_{PL} with chain length. The longer **UPy-OF*n*-UPy** has quantum yields similar to that of the **OF*n*** of the same oligomer length, while the shorter **UPy-OF*n*-UPy** has a quantum yield much lower than that of the **OF*n***.

The data above show that the bis-UPy-terminated oligomers self-assemble into supramolecular chain polymers that are still

---

(20) Eaton, D. F. *Pure Appl. Chem.* **1988**, *60*, 1107−1114.

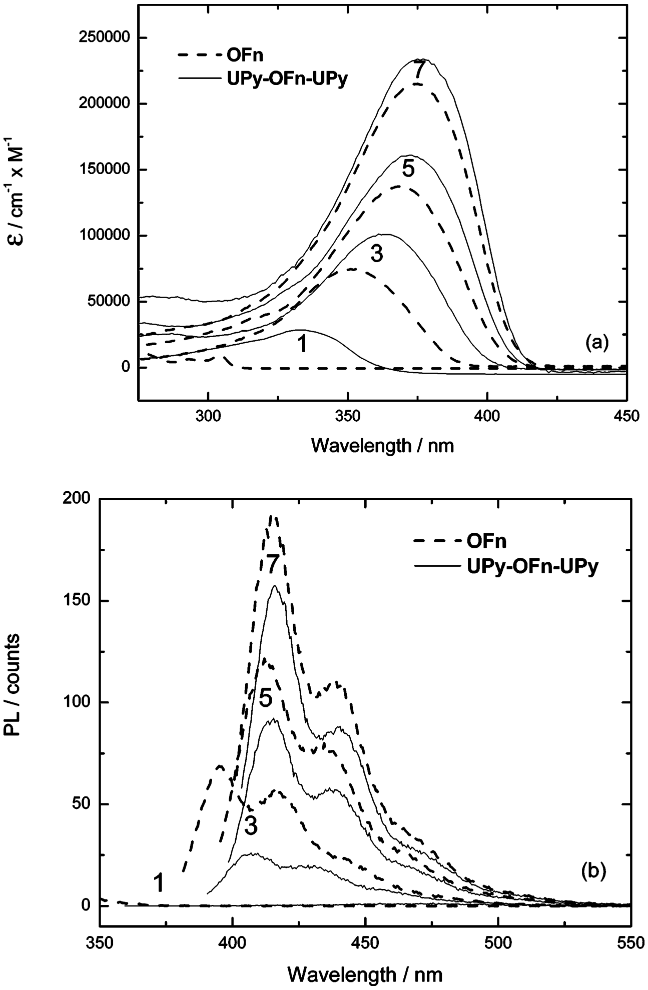


Figure 1. UV−visible (a) and fluorescence (b) spectra of oligofluorenes **UPy-OF*n*-UPy** (—) and **OF*n*** (− − −) at 6 × 10^{-7} M in $CHCl_3$. Numbers indicate oligomer length (*n*).

luminescent in solution. The degree of polymerization is high, indicating that these polymers can be processed by spin-coating.

Table 1. Summary of Absorption (λ_{max}) and Photoluminescence (PL_{max}) Spectra for Oligofluorenes in $CHCl_3$

molecule	λ_{max} (nm) ± 1	ϵ (M^{-1} cm^{-1}) ± 25%	PL_{max} (nm) ± 2	ϕ_{PL} ± 0.05	τ (ns) ± 0.2
OF1	304	9900	320	<0.01	2.0
OF3	355	75000	398	0.96	1.7
OF5	369	140000	413	0.89	1.6
OF7	375	220000	415	0.88	1.9
UPy-OF1-UPy	333	7600	391	<0.01	2.4
UPy-OF3-UPy	364	100000	407	0.30	1.9
UPy-OF5-UPy	372	160000	415	0.65	2.0
UPy-OF7-UPy	377	230000	416	0.86	2.0

Energy-Transfer Experiments

We have carried out energy-transfer experiments to adjust the emission wavelength of our hydrogen-bonded systems. Optically, oligofluorenes are blue emitters that can act as efficient energy donors when coupled with appropriate energy acceptors such as UPy-terminated green emissive oligo(*p*-phenylenevinylene) (**UPy-OPV**) and red emissive perylene bisimide (**UPy-Pery**) (Chart 1). We have used a mono-UPy-functionalized acceptor to endcap the hydrogen-bonded energy donor polymer with energy acceptors and thereby adjust the degree of polymerization. Moreover, because of the quadruple hydrogen bonds, no phase separation takes place between the donor and acceptor. Because energy transfer is strongly dependent on the distance (*d*) between donor and acceptor ($k_{et} \approx d^{-6}$), energy-transfer experiments such as these are helpful to elucidate the connectivity of supramolecular assemblies. In dilute solutions, efficient energy transfer between the donor and acceptor should be observed if two species are hydrogen-bonded. Energy-transfer experiments show that both **UPy-OPV** and **UPy-Pery** quench the fluorescence of the **UPy-OF*n*-UPy** set. For example, Figure 2a shows a series of photoluminescence spectra for a titration of **UPy-OF3-UPy** with **UPy-OPV** (see Supporting Information for an example titration with **UPy-Pery**). As expected, on addition of **UPy-OPV**, there is concomitant decrease in the fluorescence of the oligofluorene with an increase of fluorescence of the oligo(*p*-phenylenevinylene). Figure 2b summarizes this titration in a Stern−Volmer plot (▲). The calculated Stern−Volmer constant of 2.9 × 10^6 M^{-1}, which is reflecting the dimerization constant of the UPy units, is of the same order of magnitude of other Stern−Volmer constants calculated for energy-transfer experiments between UPy hydrogen-bonded donors and acceptors diads.[21] Energy transfer between **UPy-**

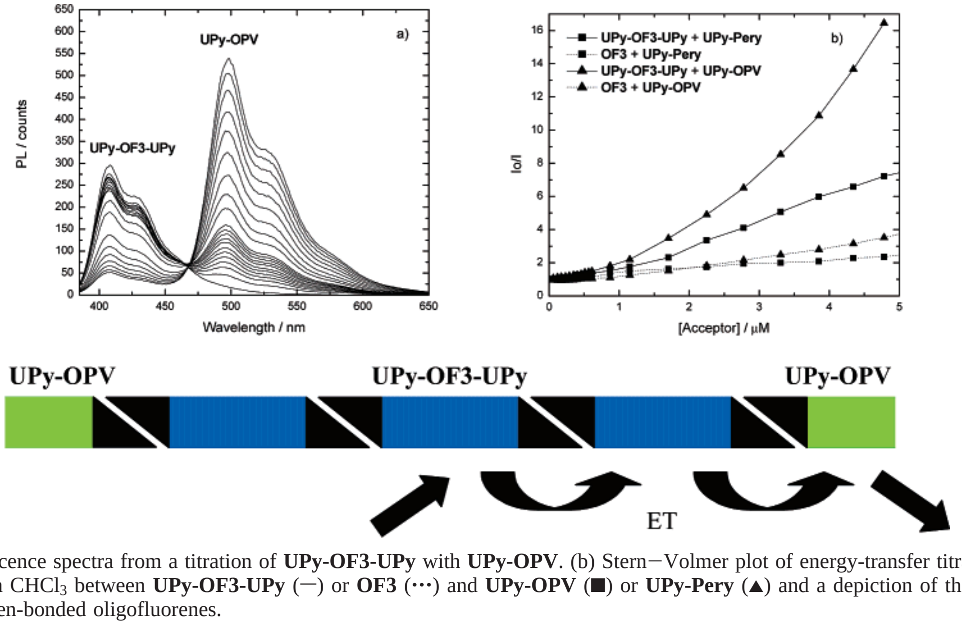


Figure 2. (a) Fluorescence spectra from a titration of **UPy-OF3-UPy** with **UPy-OPV**. (b) Stern−Volmer plot of energy-transfer titrations at 6 × 10^{-7} M donor concentration in $CHCl_3$ between **UPy-OF3-UPy** (—) or **OF3** (···) and **UPy-OPV** (■) or **UPy-Pery** (▲) and a depiction of the energy tranfer (ET) concept in the hydrogen-bonded oligofluorenes.

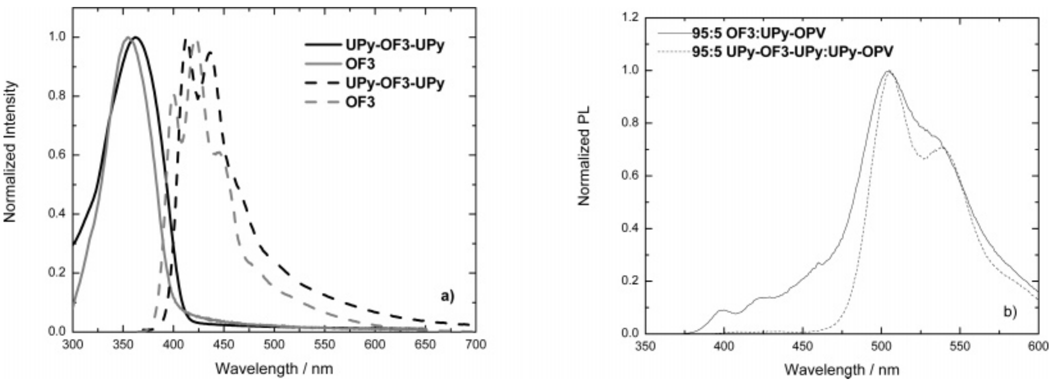


Figure 3. (a) Normalized absorption (—) and fluorescence (− − −) spectra of thin films of **UPy-OF3-UPy** (black lines) and **OF3** (gray lines) spin-coated from chloroform solutions. (b) Normalized fluorescence spectra of thin films spin-coated from solutions of 95:5 fluorene−**UPy-OPV**.

OF3-UPy and **UPy-Pery** (■; Stern−Volmer constant = 1.3×10^6 M^{-1}) is not as efficient as that between **UPy-OF3-UPy** and **UPy-OPV** as expected because of less spectral overlap: **UPy-OF3-UPy** fluoresces most strongly at 407 nm, whereas **UPy-OPV** absorbs at 436 nm and **UPy-Pery** at 515 and 553 nm (Figure 2b). Energy transfer is less than 25% as efficient if either of the donor−acceptor components lacks a hydrogen-bonding group. For example, the dotted Stern−Volmer curves in Figure 2b show Stern−Volmer plots of energy-transfer titrations between **OF3** and either **UPy-OPV** (▲, Stern−Volmer constant = 5.5 $\times$ 10^5 M^{-1}) or **UPy-Pery** (■, Stern−Volmer constant = 3.1 $\times$ 10^5 M^{-1}). At the concentration studied, hydrogen bonding seems essential for efficient energy transfer.

The energy-transfer properties of the mixed systems were also studied in thin films. As expected for supramolecular polymers, solutions of bis-UPy-terminated oligofluorene could be easily spin-coated on glass yielding smooth films. Figure 3a shows the normalized absorbance and fluorescence spectra of thin films of **OF3** and **UPy-OF3-UPy** deposited from chloroform. The peak positions of maximum absorption are the same in solution as in the solid state for both samples, but the emission maxima shift bathochromically from solution to solid state (Figure 3). When a small amount (5%) of **UPy-OPV** was mixed with either **OF3** or **UPy-OF3-UPy,** the fluorescence of the **UPy-OF3-UPy** is completely quenched, indicating efficient energy transfer to the oligo(phenylenevinylene) in the solid state (Figure 3b), while in the case of **OF3**, incomplete fluorescence quenching is observed (Figure 3b).

Conclusion and Outlook

In conclusion, we have developed a new class of supramolecular π-conjugated polymers: oligomers of fluorene of four different lengths that are noncovalently connected by quadruple hydrogen bonds to form polymers. ^{1}H NMR spectroscopy and the resulting material properties indicate that bis-ureidopyrimidinone-terminated oligofluorenes do indeed form supramolecular polymers. The synthesis described here to functionalize the ends of oligofluorenes is general and should permit construction of even longer UPy-oligofluorenes as well as the synthesis of other supramolecular π-conjugated polymers such as those made from oligothiophenes. The resulting UPy-terminated oligofluorenes are modular and can be readily endcapped by simple addition of mono-UPy-terminated groups. Supramolecular co-block polymers should be possible by mixing of two bis-UPy-terminated monomers. We have capped the UPy-terminated oligofluorenes with energy acceptors UPy-perylenebisimides and UPy-oligo(*p*-phenylenevinylene) to show that these oligofluorenes can act as energy donors and that hydrogen bonding enhances energy transfer. Because of their advantageous electronic and material properties, noncovalently connected oligofluorenes are promising candidates for light-emitting diodes.

Acknowledgment. We thank Dr. X. Lou for MALDI-TOF analyses, Rint Sijbesma and Rene Janssen for helpful discussions on hydrogen-bond assemblies and energy transfer, and Dorothee Wasserberg for determination of quantum yields. This work, as part of the European Science Foundation EUROCORES Programme SONS, was supported by funds form The Netherlands Organization for Scientific Research (NWO) and the EC Sixth Framework Programme.

Supporting Information Available: Synthesis and characterization of all intermediates, hydrogen-terminated oligofluorenes (**OF*n***), and UPy-terminated oligofluorenes (**UPy-OF*n*-UPy**), **UPy-OPV**, and **UPy-Pery**, ^{1}H NMR spectra of **UPy-OF*n*-UPy**, and energy-transfer titration plots. This material is available free of charge via the Internet at http://pubs.acs.org.

JA052054K

---

(21) Neuteboom, E. E.; Beckers, E. H. A.; Meskers, S. C. J.; Meijer, E. W.; Janssen, R. A. J. *Org. Biomol. Chem.* **2003**, *1*, 198−203.