COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Monodisperse fluorene oligomers exhibiting strong dipolar coupling interactions

Rémi Anémian,[a] Jean-Christophe Mulatier,[a] Chantal Andraud,*[a] Olivier Stéphan[b] and Jean-Claude Vial[b]

[a] *Laboratoire de Stéréochimie et Interactions Moléculaires, ENS-Lyon and CNRS, 46 Allée d'Italie, 69364 Lyon cédex 07, France. E-mail: Chantal.Andraud@ens-lyon.fr*

[b] *Laboratoire de Spectrométrie Physique, Université Joseph Fourier and CNRS, 140 rue de la physique, BP 87 38402 Saint Martin d'Hères cédex, France*

Received (in Corvallis, OR, USA) 8th February 2002, Accepted 29th May 2002
First published as an Advance Article on the web 26th June 2002

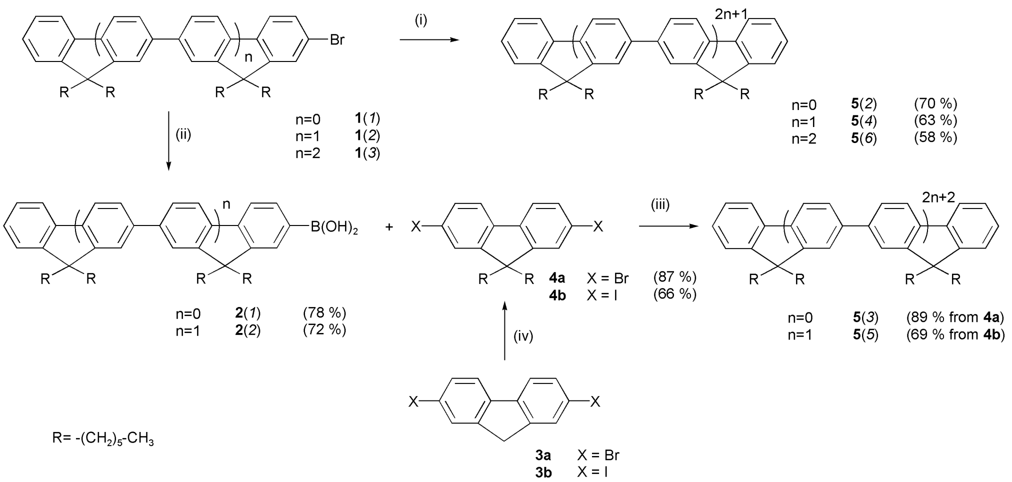
Well-defined fluorene oligomers (n = 1 to 6) were prepared step by step using Suzuki and Yamamoto couplings, while absorption and photoluminescence properties evidenced very large dipolar coupling interactions between fluorene moieties.

Monodisperse systems are more than models providing structure–property relationships in order to rationalise behaviour of high weight polymers.[1] Thus, research focusing on conjugated oligomers is also of current interest to investigate efficient materials for electronics and photonics applications.[2] In this field, recent reports have shown the oligomer approach to be promising in the design of optimised systems for two-photon absorption (TPA) based applications. A theoretical study of various conjugated oligomers has shown that their TPA amplitude could arise from a large enhancement of the transition dipole moments when compared to that of the corresponding monomer.[3] This special feature was ascribed to coupling interactions between monomers as in the excitonic model of Kasha.[4] In this context we have already reported that bifluorene derivatives exhibit very promising experimental TPA induced optical limiting properties.[5] An even more pronounced effect was obtained with high molecular weight, *i.e.* number-average molecular weight close to 20 000 Da, poly(dihexyl)fluorene (denoted 60-PDHF ; 60 fluorene units) leading to tremendous TPA efficiencies in the visible range when compared to other organic systems.[6] Assuming that TPA should result from dipolar coupling effects monodisperse fluorene oligomers were prepared to validate the coupling assumption.

Although monodisperse oligofluorenes have been already isolated *via* a random approach by means of high pressure liquid chromatography of an oligomeric mixture,[7] no systematic synthesis of the fluorene series has been reported. The notation for our oligofluorene derivatives will consist in two parameters $N(n)$ in which N and n represent respectively the number of the oligofluorene series and the number of fluorene units in the series (Scheme 1). First of all, hexyl chains were introduced at the C9 position of each fluorene unit to reach high solubility in classical organic solvents.[6] The compound **5**(1) was directly prepared in 97% yield by alkylation of the commercially available fluorene with 1-bromohexane in the presence of anhydrous potassium *tert*-butylate. Our general synthetic strategy for longer oligomers was based on a step-by-step growth methodology using cross-coupling reactions leading to the formation of oligomers **5**(n) up to n = 6 with yields ranging from 58% to 89% (Scheme 1).

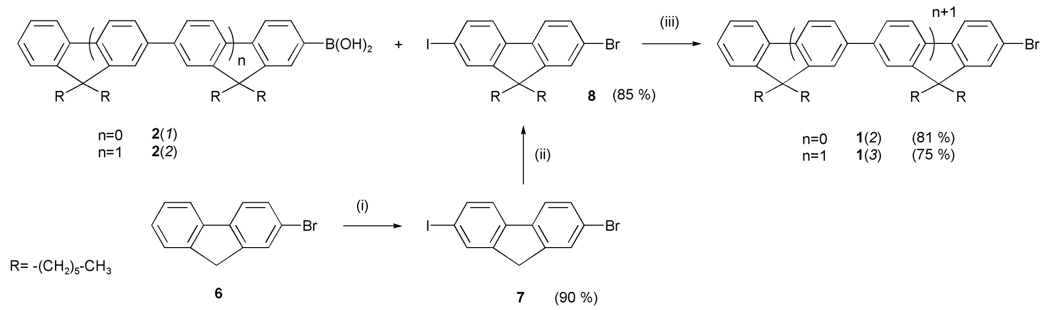
Oligomers **5**(2), **5**(4), **5**(6) were obtained respectively from the homocoupling of the 2-bromo-oligo(9,9-dihexyl)fluorenes **1**(1), **1**(2) and **1**(3) using a Yamamoto procedure.[8] Odd oligomers **5**(3) and **5**(5) were prepared from the condensation of the 2-oligo(9,9-dihexylfluorenyl)boronic acids **2**(1) and **2**(2) with compounds **4a** or **4b** *via* a Suzuki cross-coupling reaction.[9] Compounds **2**(1) and **2**(2) were obtained directly from the 2-bromo-oligo(9,9-dihexyl)fluorenes **1**(1) and **1**(2) after conversion to their corresponding lithium derivatives and reaction with triisopropoxyborane. The key compounds of this strategy were the 2-bromo-oligo(9,9-dihexyl)fluorenes **1**(1), **1**(2) and **1**(3); their synthesis is reported in Scheme 2.

Alkylation of the commercially available 2-bromofluorene **6** led to the first compound of the series **1**(1), while higher homologous **1**(2) and **1**(3) were obtained from the coupling of the 2-oligo(9,9-dihexylfluorenyl)boronic acids **2**(1) and **2**(2) respectively with **8** *via* a Suzuki reaction, in which the coupling on the iodo site is significantly faster, leaving the bromo unreacted.[10] All compounds were characterised by NMR



Scheme 1 *Reagents and conditions*: (i) $P(Ph)_3$, Zn powder, 2,2′-dipyridyl, $NiCl_2$, *N,N*-dimethylacetamide, 80 °C, 48 h; (ii) a. BuLi (2,5 M), TMEDA, anhydrous toluene, rt, 2 h. b. $B(OCH(CH_3)_2)_3$, anhydrous toluene, RT, 12 h. c. HCl (2 M), 30 min; (iii) $Pd(P(Ph)_3)_4$, Na_2CO_3 (2 M), anhydrous toluene, 80 °C, 2 days; (iv) *t*-BuOK, 1-bromohexane, anhydrous DMF, 40 °C, 18 h.

DOI: 10.1039/b201414a



Scheme 2 *Reagents and conditions* (i) I_2, HIO_3, H_2SO_4, CCl_4, 80 °C, 4 h; (ii) *t*-BuOK, 1-bromohexane, anhydrous DMF, 40 °C, 18 h; (iii) $Pd(P(Ph)_3)_4$, Na_2CO_3 (2 M), anhydrous toluene, 80 °C, 2 days.

Table 1 Optical properties of polyfluorenes **5**(*n*)

n	λ_{abs} (nm)[a]	λ_{lum} (nm)[b]	ε (L mol^{-1}cm^{-1})	μ_n (D)[c]	τ (ns)[d]
2	330	370	53570	6.6	1.030
3	352	400	90975	9.2	0.812
4	364	411	124350	10.7	0.760
5	370	416	147050	12.3	0.650
6	375	418	173870	13.1	0.604

[a] In dichloromethane. [b] In $CHCl_3$; zero phonon peak. [c] μ_n was derived from absorption spectra. [d] A short rise time followed by exponential decay was obtained from the laser femtosecond mode with a time resolution of 50 ps.

spectroscopy, elemental analysis and/or mass spectrometry and found to be in good agreement with expected structures.

All oligomers **5**(*n*) show an intense absorption in the UV region, while photoluminescence spectra, obtained by excitation at 310 nm from the second harmonic of a Ti laser, consist in structured bands (vibronic spacing about 1200 cm^{-1}). Optical properties of these polyfluorenes depend strongly on the length of the molecule (Table 1) and could be rationalised in the following in terms of coupling interactions. Absorption energies decrease with n following the quantum-mechanical law eqn. (1) of Davidov

$$E_{01}(n) = A - 2\left|M\right|\cos\frac{\pi}{n+1} \qquad (1)$$

based on monomer interactions in oligomers, in which A and M are respectively the fluorene energy and the interaction matrix.[11] Moreover, the experimental energy value obtained for the 60-PDHF polyfluorene (3.20 eV)[6] is compatible with the infinite extrapolation energy (3.19 eV) found when using the relationship (1) and led to a conjugation effective length of n = 11 in good agreement with previous data.[7] An exponential dependence of type given in eqn. (2)

$$\mu_n = n^{\alpha}\mu_1 \qquad (2)$$

between the transition dipole moments μ_n of the oligomer **5**(*n*) and μ_1 of the fluorene unit was determined from absorption spectra with $\alpha = 0.7$ in excellent correlation with the Kasha aggregate model ($\alpha = 0.5$).[4]† Moreover photoluminescence intensities were found to decay exponentially (100 femtosecond excitation pulse at 360 nm; detection at λ_{lums}) due to the well-defined structure of polyfluorenes with very short lifetimes in the sub-nanosecond range. The oligofluorenes high luminescence quantum efficiency *QE* ranging from 0.9 to 1, measured by means of an etalon, allows the approximation eqn. (3)

$$QE = W_r/(W_r + W_{nr}) \approx 1 \qquad (3)$$

and leads to relate directly their fast decay times τ to the radiative rate W_r according to eqn. (4)

$$\tau = 1/((W_r + W_{nr}) \propto \frac{1}{W_r} = \frac{3\varepsilon_0 hc^3}{\omega^3(\mu_n)^2} \qquad (4)$$

in which ω is the emission frequency. It is noteworthy that the nonradiative rate W_{nr} was neglected. Due to the bathochromic shift of ω (Table 1), the strong decrease of τ with n can be ascribed to the high enhancement of μ_n (eqn. (1)).

In conclusion, coupling interactions were shown strongly to control physical properties of polyfluorene-based materials such as absorption and luminescence decay times by generation of large transition dipole moment values. Although energy transfer processes have been previously assumed in dendrimers, no direct correlation with physical properties of these systems was established.[12] Recent calculations on optical properties of other different oligomer families could allow the generalization of this behaviour.[13] This trend makes the oligomer approach very attractive in several nonlinear optic fields according to the possible optimisation of nonlinearity–transparency trade-off assuming that all studied polyfluorenes (up to 60-PDHF) absorb in the visible. In that context, the synthesis of longer oligomers ($n > 6$) is in progress to complete the series. The TPA properties of polyfluorenes **5**(*n*) will be also investigated in detail.

Notes and references

† The difference between the Kasha and the experimental exponent values arises from conjugation effects, which should be weak due to the non-coplanarity of the different fluorene moities.

1 R. E. Martin and F. Diederich, *Angew. Chem., Int. Ed.*, 1999, **38**, 1350.
2 *Electronic Materials: The Oligomer Approach*, eds. K. Müllen and G. Wegner, Wiley VCH, Weinheim, 1998.
3 C. Andraud and P. L. Baldeck, *Nonlinear Optics*, 2000, **25**, 133.
4 E. G. McRae and M. Kasha, *J. Chem. Phys.*, 1958, **28**, 721.
5 Y. Morel, A. Irimia, P. Najechalski, O. Stephan, P. L. Baldeck and C. Andraud, *J. Chem.Phys.*, 2001, **114**, 5391.
6 P. Najechalski, Y. Morel, O. Stéphan and P. L. Baldeck, *Chem. Phys. Lett.*, 2001, **343**, 44.
7 G. Klaerner and R. D. Miller, *Macromolecules*, 1998, **31**, 2007.
8 T. Yamamoto, Y. Hayashi and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 209.
9 N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457.
10 G. W. Gray, M. Hird, D. Lacey and K. J. Toyne, *J. Chem. Soc., Perkin Trans. 2*, 1989, 2041.
11 A. S. Davidov, *Zh. Eksp. Teor. Fiz.*, 1948, **18**, 515; *Theory and Applications of Ultraviolet Spectroscopy*, eds. H.H. Jaffé and M. Orchin, Wiley, NY, 1964.
12 M. Drobizhev, A. Rebane, C. Sigel, E. H. Elandaloussi and C. W. Spangler, *Chem. Phys. Lett.*, 2000, **325**, 375.
13 R. Anémian, P. Baldeck, N. Plé, and C. Andraud: manuscript on theoretical TPA properties of various oligomers in preparation.