Synthesis and Photophysical Properties of a Highly Fluorescent Ditopic Ligand Based on 1,6-Bis(ethynyl)pyrene as Central Aromatic Core

Stéphanie Leroy-Lhez*[a] and Frédéric Fages*[b]

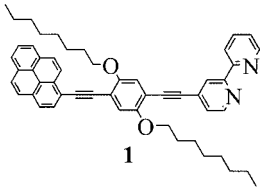
Keywords: Pyrene / 2,2′-Bipyridine / Fluorescence / Synthesis / Conjugated oligomer

A simple synthetic route for the efficient preparation and purification of two regioisomers of a pyrene derivative containing two ethynyl groups—1,6- and 1,8-bis(ethynyl)pyrene—is described. The former compound was used as a building block for the stepwise synthesis of a highly conjugated, ditopic bis(2,2′-bipyridine) ligand (**2**) containing the pyrene nucleus at the central core. The fluorescence properties of ligand **2** are reported.

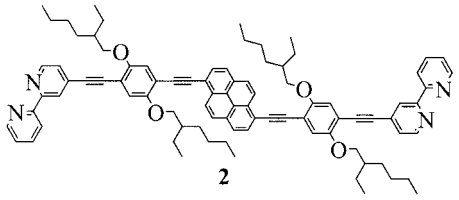
Introduction

Ever since it was first isolated from coal tar in 1837,[1] pyrene has been the subject of tremendous investigation. Indeed, this polycyclic aromatic hydrocarbon exhibits a set of many interesting electrochemical[2] and photophysical[3] attributes, which have resulted in its utilization in a variety of scientific areas. Some recent advanced applications of pyrene include fluorescence labeling of oligonucleotides for DNA assay,[4] electrochemically generated luminescence,[5] carbon nanotube functionalization,[6] fluorescence chemosensing,[7] design of luminescent liquid crystals,[8] supramolecular self-assembly,[9] etc.

Pyrene-containing receptors for transition metal ions were recently reported as a versatile class of photoactive supramolecular systems.[10–12] In that connection, we had reported previously on dyad and triad molecules in which pyren-1-yl or pyrene-1,6-diyl units, respectively, are connected to the 2,2′-bipyridine (bpy) moiety by a single C–C bond.[13,14,17] Recently, rod-like bpy-pyrene dyads, such as compound **1**, containing a phenylene ethynylene unit as rigid bridge were shown to display outstanding photophysical features owing to extended conjugation.[15,16] In particular, the singlet and triplet excited state properties of **1** were found to be dramatically sensitive to the binding of metal ions, such as zinc(II) and ruthenium(II). This prompted us to synthesize the related ditopic ligand **2**, in which the central pyrene ring is symmetrically substituted in the 1,6-positions with two bpy-terminated phenylene ethynylene segments. As such, triad **2** was anticipated to act not only as a nanoscale fluorophore,[17] but also as a rigid photonic wire for the bridging of two luminophoric transition metal centers.[18] Polyaromatic systems have been used as energy relay subunits within conjugated backbones.[19] Moreover, conjugated oligomers and polymers incorporating ligand units have received great attention as photoconducting, photonic, or sensory materials.[20]



1



2

Critical to the synthesis of ligand **2** is the efficient preparation of the acetylenic precursor 1,6-bis(ethynyl)pyrene (**5A**; Scheme 2, below), which requires regiochemical control of the aromatic substitution on the pyrene ring. Direct electrophilic substitution occurs exclusively at the electron-rich 1-, 2-, 3-, and 4-positions, affording isomeric mixtures in variable ratios depending on the experimental conditions. Friedel–Crafts monoacetylation of pyrene is known to afford the 1-substituted monoacetyl derivative specifically unless an excess of acetyl chloride is used. In the latter case the 1,3-, 1,6-, and 1,8-diacetyl isomers are formed and can be separated by a sequence of tedious purification steps involving both chromatography and crystallization.[21] Similarly, dibromination of pyrene with Br_2 gives a mixture of

[a] CIMMA UMR 6200 CNRS, Université d'Angers,
2 Bd Lavoisier, 49045 Angers Cedex, France
Fax: +33-2-41-73-54-05
E-mail: stephanie.lhez@univ-angers.fr
[b] GCOM2 UMR 6114 CNRS, Université de La Méditerranée,
Faculté des Sciences de Luminy
Case 901,
13288 Marseille Cedex 9, France
E-mail: fages@luminy.univ-mrs.fr

  DOI: 10.1002/ejoc.200500059

1,6- and 1,8-dibromopyrenes, which can be resolved by fractional crystallization.[22] In our hands, this method offered the less soluble 1,6-bromopyrene in pure form but low yield, but not the pure 1,8-isomer.[14] In addition, 2,7-substituted pyrenes also represent attractive scaffolds on which to base the design of conjugated oligomers with a well defined straight shape.[23] These, however, are much less soluble, unless alkyl chains are introduced at the 4- and 9-positions, and substitution at the 2,7-positions of pyrene requires tedious indirect routes.,[24,25] Moreover, the molecular orbital coefficients of the 2- and 7-centers are nearly zero, which induces electronic decoupling of the pyrene ring with the π-delocalized substituent. Although this peculiar property may impart new electronic features to the conjugated rods, it has scarcely been investigated so far.[26]

Here we report an efficient and expeditious method allowing both the pure 1,6- and 1,8-isomers of bis(ethynyl)-pyrene, **5A** and **5B**, respectively, to be obtained in good yield as precursors of phenylene ethynylene-based conjugated systems. The synthesis of the ditopic ligand **2** from **5A** is described. Photophysical measurements show that **2** strongly absorbs and emits in the visible region.

Results and Discussion

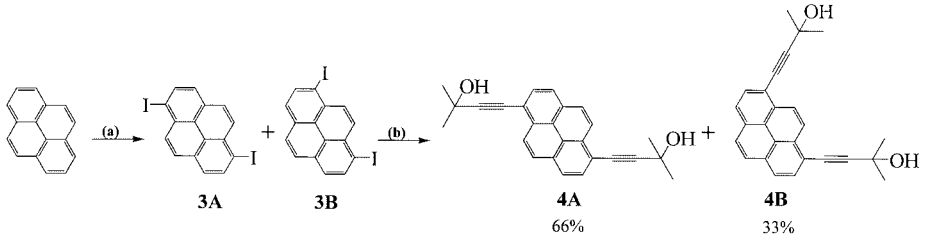
Synthesis

The synthetic route to triad **2** involved iodination of pyrene by a standard procedure,[27,28] which afforded a mixture of the 1,6- and 1,8-diiodo derivatives in a 7:3 ratio according to ^{1}H NMR spectroscopy (Scheme 1). Several attempts to resolve the two regioisomers by crystallization were unsuccessful. Eventually the mixture was directly subjected to an ethynylation reaction, under Sonogashira conditions, with 2-methylbut-3-yn-2-ol, which resulted in the formation of the corresponding diols **4A** and **4B** (Scheme 1). It was anticipated that the divergent or convergent orientations of the hydrogen-bonding hydroxy functions in **4A** or **4B**, respectively, could endow such compounds with markedly different solubility properties in organic solvents. Indeed, the somewhat more centrosymmetric compound **4A** was found to be much less soluble than its 1,8-isomer, precipitating almost quantitatively upon trituration of the crude product with dichloromethane. After filtration, compound **4A**, obtained in 21% overall yield from pyrene, could be used in the following step without further purification. Column chromatography of the soluble fraction allowed the 1,8-isomer to be obtained in pure form.

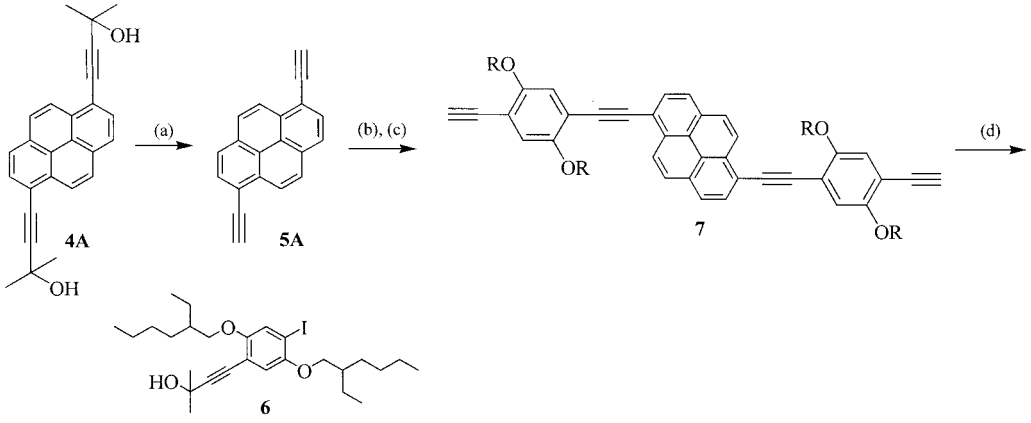
After conventional treatment under basic conditions, compounds **4A** and **4B** yielded the corresponding bis(ethynyl)pyrene derivatives **5A** and **5B**, respectively. 1,6-Bis(ethynyl)pyrene **(5A)** afforded oligomer **2** after a sequence of Pd-mediated cross-coupling reactions of ethynyl derivatives with the corresponding haloarenes (Scheme 2), similarly to the synthetic route previously described for compound **1**.[15] Thanks to the presence of branched alkyl chains, compound **2** is soluble in common organic solvents.

Spectroscopic Properties

Triad compound **2** does indeed behave as a strongly visible absorbing and emitting chromophore in fluid solution



Scheme 1. a) I_2/KIO_3 (1 and 0.4 equiv.), $CH_3COOH/H_2O/H_2SO_4$ (100:10:1 ratio), 40 °C, 4 h, 32%. b) $HC{\equiv}C(CH_3)_2OH$ (2.3 equiv.), Et_2NH, $[Pd^{II}(PPh_3)_2Cl_2]$ (2.2 mol%), CuI (2.8 mol%), 50 °C, 20 h.



Scheme 2. a) NaOH (9 equiv.), toluene, reflux, 3 h, 58%. b) Compound **6** (2 equiv.), Et_2NH, $[Pd^{II}(PPh_3)_2Cl_2]$ (10 mol%), CuI (10 mol%), 50 °C, 20 h, 61%. c) KOH (13 equiv.), toluene, reflux, 1 h, 53%. d) 4-Bromo-2,2′-bipyridine (2.2 equiv.), toluene, iPr_2NH, $[Pd(PPh_3)_4]$ (13 mol%), 80 °C, 24 h, 61%.

at room temperature. Indeed, its absorption maximum for the lowest-energy transition band is red-shifted by about 60 nm relative to dyad **1** (Table 1, Figure 1) and the molar absorption coefficient is nearly twice as high as that of **1** at the maximum wavelength.[15] The oscillator strength, calculated with the assumption of a single transition for the lowest-energy absorption,[14,15] is 2.42 in THF as solvent, which is remarkably high in comparison with the value obtained for **1** (0.80).[15b] The electronic absorption features of **2** were found to be independent of the solvent polarity. This observation, indicative of the absence of any significant charge transfer in the ground state, is in agreement with previous observations on bpy-pyrene ligands.[14,15] Moreover the longest-wavelength absorption band is observed to be more structured than those of monosubstituted pyrene analogue derivatives.

Table 1. Photophysical properties of ligands **1** and **2** at room temperature in toluene and THF; "–" = not determined.

	Ligand **2**		Ligand **1**[15b]	
	Toluene	THF	Toluene	THF
ε [$M^{-1}{\cdot}cm^{-1}$]	78300	94600	47600	52600
λ_{max} (abs.)	462, 441	461, 440	411	411
λ_{max} (em.)	478	480	443	443
$\Delta\nu$ [cm^{-1}]	703	837	1760	1760
Φ_{fluo}	0.50	0.60	0.52	0.68
τ [ns]	–	1.0	–	1.7
k_f [$10^8\ s^{-1}$]	–	6.0	–	4.0
$k_f/\nu_f^3 n^3$ [$10^{-5}\ s^{-1}{\cdot}cm^3$]	–	2.4	–	1.3

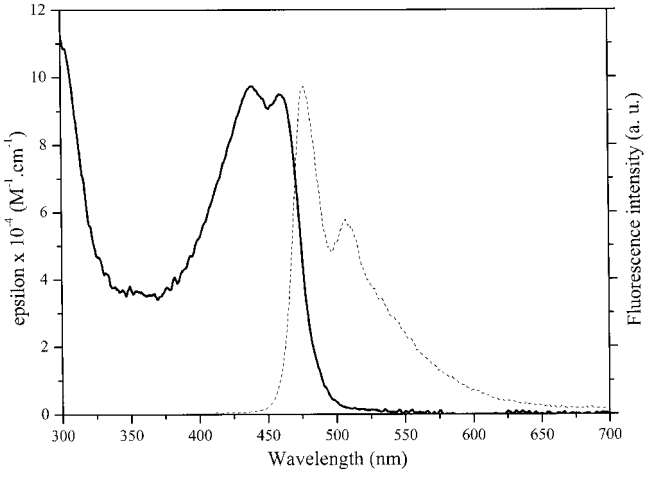


Figure 1. Absorption (–) and corrected fluorescence emission (···) spectra of **2** in THF at room temperature (c = ca. 3×10^{-6} mol·L^{-1}).

The corrected fluorescence emission spectrum of **2** (Figure 1 and Table 1) was found to be independent both of the polarity of the solvent and of the excitation wavelength. The fluorescence excitation spectrum matched the absorption profile over the entire wavelength range. Consistently with the case of monobpy-pyrene systems, the fluorescence emission spectrum of **2** displays a clear vibrational structure. The vibronic spacing is found to be ca. 1300 cm^{-1}, which is in agreement with the stretching modes of the aromatic pyrene nucleus.[15b] The Stokes' shift values in both toluene and THF are in the 700–850 cm^{-1} range and so are significantly lower than those obtained for ligand **1** (1760 cm^{-1} in both solvents). These results, together with those obtained from electronic absorption spectroscopy, point to **2** having a more rigid structure than **1** in both the ground and the excited states. Compound **2** is strongly emissive in the visible region, as evidenced by the high value of the fluorescence quantum yield (Table 1). The excited state of **2** was observed to decay monoexponentially and to display a very short fluorescence lifetime (1 ns in THF). The radiative rate constants—k_f and its reduced value $k_f/n^3\nu_f^3$, which takes the wavelength dependence on the emission probability in account—were calculated in THF (Table 1). Both values were found to be higher for **2** than for **1**. All together, the photophysical data obtained for **2** are consistent with the occurrence of a highly allowed ππ* singlet excited state in which the excited state of the pyrene chromophore exhibits a strong ^1L_a character. Moreover, such stabilization of the long-axis polarized transition seems to be more effective in the case of disubstitution at the 1- and 6-positions of the pyrene nucleus.

Conclusions

We have described a very efficient method to introduce a pyrene chromophore in the central core of a phenylene ethynylene oligomer. The approach relies on the functionalization of a mixture of 1,6- and 1,8-dihalogenated pyrene derivatives with 2-methylbut-3-yn-2-ol under Sonogashira conditions. The resulting mixture of dialcohol isomers is simply resolved by crystallization, to yield the 1,6- and 1,8-bis(ethynyl)pyrene difunctional building blocks. As an example, the use of the 1,6-isomer allowed to us construct the conjugated ditopic ligand **2**, which exhibits an intense visible fluorescence emission. Use of the same precursor for the preparation of conjugated polymers with unique photophysical properties could also be envisaged. Moreover, the 1,8-isomer, also obtained in this study, could represent a precursor of choice for the generation of conjugated macrocycles.

Experimental Section

General Remarks: All solvents used for spectroscopic measurements were of spectroscopic grade and were used as commercially available. Electronic absorption spectra were recorded with a Hitachi U3300 spectrophotometer. The integrated absorption intensity, $\int\varepsilon d\nu_a$, which is proportional to the oscillator strength (f) was calculated from the absorption spectra for the lowest-energy transition. Fluorescence spectra were recorded in nondeoxygenated solvents at 20 °C with either a Hitachi F4500 or a Spex Fluorolog spectrofluorimeter. We did not find any difference in emission properties with or without degassing the solutions. Fluorescence quantum yields were determined with quinine sulfate as a standard (Φ_f = 0.55 at 25 °C in 1 N H_2SO_4). The relative error in the quantum yields is ±5%. The laser setup used in these experiments consists of a hybrid mode-locked dye laser associated with an actively

mode-locked cw-pumped Nd:YAG laser (Coherent "Antares 76-S"), a dye amplifier and a Nd:YAG regenerative amplifier. Pulses of 1 ps (1 mJ, 10 Hz repetition rate) tuned to 600 nm were generated. The samples were excited with 1 ps pulses at 300 nm generated by frequency doubling of the fundamental 600 nm laser pulse in a KDP crystal. Fluorescence was collected by use of achromatic lenses and detected through a polarizer set at magic angle (54.7°) with a Hamamatsu C5680 streak camera and a Chromex 250IS spectrograph.

All chemicals were purchased from Aldrich Chemical Co. and were used as received. Solvents were distilled prior to use. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AC 200 or a Bruker AC 250 spectrometer. Mass spectra were obtained with a VG Autospec-Q Micromass spectrometer either in the EI or the LSIM$^+$ (NBA matrix) mode.

Diiodopyrene (3A, 3B): Pyrene (12 g, 59.3 mmol) was dissolved in acetic acid (400 mL) at 90 °C. The reaction mixture was cooled to 40 °C, and then water (40 mL), iodine (15.07 g, 59.36 mmol), potassium iodate (5.14 g, 24 mmol), and concentrated H_2SO_4 (4 mL) were added. The mixture was stirred at 40 °C for 4 h. The brown solid was filtered, washed with dichloromethane and water, and dried under vacuum to afford **3A** and **3B** as a mixture after recrystallization from hot toluene (8.8 g, 32% yield). M.p. 120–140 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.92 (d, J = 8.1 Hz, 2 H, H^3 and H^8), 8.1 (d, J = 9.1 Hz, 2 H, H^4 and H^9), 8.34 (d, J = 9.1 Hz, 2 H, H^5 and H^{10}), 8.54 (d, J = 8.1 Hz, 2 H, H^2 and H^7) ppm for **3A**. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.91 (d, J = 8.1 Hz, 2 H, H^3 and H^6), 8.07 (s, 2 H, H^4 and H^5), 8.39 (s, 2 H, H^9 and H^{10}), 8,54 (d, J = 8.2 Hz, 2 H, H^2 and H^7) ppm for **3B**.

Disubstituted Pyrene (4A, 4B): A Schlenk flask was charged with a solution of 2-methyl-but-3-yn-2-ol (1 mL, 10.3 mmol) in freshly distilled diethylamine (60 mL). The solution was freeze–pump–thaw degassed and transferred to a mixture of **3A** and **3B** (2 g, 4.4 mmol), Pd[PPh$_3$]$_2$Cl$_2$ (68 mg), and CuI (0.12 mmol) under argon atmosphere. The reaction mixture was heated at 50 °C under argon atmosphere for 20 h. The solvent was removed under vacuum and the insoluble product was filtered, washed with dichloromethane, and dried. Compound **4A** was obtained as a brownish solid (1.07 g, 66%). The filtrate was evaporated and the crude product was then subjected to column chromatography (silica gel) with elution with dichloromethane/methanol (0 to 1%). Compound **4B** was obtained as a yellow solid (538 mg, 33% yield).

Compound 4A: M.p. 237–238 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.81 (s, 12 H, CH_3), 8.09–8.13 (m, 6 H, H^{pyr}), 8.52 (d, J = 9.1 Hz, 2 H, H^2 and H^7) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 32.1 (CH_3), 82.4 (C≡C), 82.9 (C≡C), 117.2, 125.0, 126.2, 128.2, 130.4, 131.3, 132.4, 132.7 ppm. MS (EI): m/z: 366 [M]$^+$. Analysis: calcd. (found) for $C_{26}H_{22}O_2$ (198): C 85.24 (83.91), H, 6.01 (6.06).

Compound 4B: M.p. 95–100 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.80 (s, 12 H, CH_3), 8.04 (s, 2 H, H^3 and H^6), 8.11 (s, 4 H, H^4, H^5, H^9 and H^{10}), 8.60 (s, 2 H, H^2 and H^7) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 31.8 (CH_3), 66.1 (–C–C≡C), 81.1 (C≡C), 100 (C≡C), 117.9, 125.0, 126.2, 127.9, 131.3, 132.8 ppm. MS (EI), m/z: 366 [M]$^+$; Analysis: calcd. (found) for $C_{26}H_{22}O_2$ (198): C 85.24 (84.10), H 6.01 (6.02)%.

1,6-Diethynyl-pyrene (5A): A solution of **4A** (500 mg, 1.34 mmol) and NaOH (480 mg, 12 mmol) in freshly distilled toluene (20 mL) was heated at reflux for 3 h. This solution was filtered while hot. After cooling down to room temperature, the organic layer was washed with water until pH = 7 and dried over sodium sulfate, and the solvents were evaporated. The crude product was recrystallized from hot toluene to afford **5A** as brown needles (200 mg, 58% yield). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.64 (s, 2 H, C≡C–*H*), 8.13–8.22 (m, 6 H, H^{pyr}), 8.62 (d, 2 H, J = 9.1 Hz, H^2 and H^7) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 83.0 (C≡C), 125.1, 126.3, 128.3, 130.6 ppm. MS (EI), m/z: 250 [M]$^+$.

Diethynyl Compound (7): A solution of **5A** (0.401 g, 1.6 mmol), **6** (1.701 g, 3.13 mmol), and freshly distilled diethylamine (50 mL) was freeze–pump–thaw-degassed and transferred to a mixture of Pd[PPh$_3$]$_2$Cl$_2$ (115.5 mg, 0.16 mmol) and CuI (30.8 mg, 0.16 mmol) under argon atmosphere. The reaction mixture was heated at 50 °C for 20 h under inert atmosphere. After the mixture had cooled down to room temperature, the solvent was removed under vacuum. The crude product obtained was dissolved in dichloromethane and filtered. The filtrate was concentrated and purified by chromatography on a silica gel column, with elution with dichloromethane, to yield the coupling product as an orange solid (1.03 g, 61% yield). M.p. 150 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.85–1.03 (m, 24 H, CH_3), 1.2–1.85 (m, 44 H, –CH_2–), 1.66 [s, 12 H, C(CH_3)$_2$], 3.93–4.0 (m, 8 H, –O–CH_2), 7.0 (s, 2 H, H^{phen}), 7.14 (s, 2 H, H^{phen}), 8.10–8.21 (m, 6 H, H^{pyr}), 8.80 (d, J = 9 Hz, 1 Hz, 2 H, H^2 and H^7) ppm. MS (LSIMS$^+$), m/z: 1079 [M]$^+$. Analysis: calcd. (found) for $C_{74}H_{94}O_6$ (1078): C 82.33 (82.65), H 8.78 (8.72)%.

A mixture of this protected compound (380 mg, 0.35 mmol) and KOH (260 mg, 4.63 mmol) in toluene (20 mL) was heated at reflux for 1 h and was then filtered. The filtrate was washed with water until pH 7. The organic layer was dried over Na_2SO_4. After removal of the solvent, the crude product was purified by column chromatography (silica gel), with elution with petroleum ether/dichloromethane (1 to 25%) to yield **7** as a yellow oil (0.180 g, 53% yield). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.80–1.05 (m, 24 H, CH_3), 1.2–2.0 (m, 44 H, CH_2), 3.37 (s, 2 H, C≡CH), 3.95–4.05 (m, 8 H, OCH_2), 7.06 (s, 2 H, H^{phen}), 7.17 (s, 2 H, H^{phen}), 8.12–8.21 (m, 6 H, H^{pyr}), 8.81 (d, J = 9.1 Hz, 2 H, H^2 and H^7) ppm. MS (LSIMS$^+$), m/z: 963 [M + 1]$^+$.

Bis-bipyridine Pyrene Ligand (2): A solution of **7** (150 mg, 0.15 mmol) and 4-bromo-2,2′-bipyridine (78 mg, 0.33 mmol) in freshly distilled toluene (10 mL) and diisopropylamine (4 mL) was freeze–pump–thaw degassed and transferred by cannula to the catalyst Pd[PPh$_3$]$_4$ (23 mg, 0.02 mmol) under argon. The reaction mixture was heated at 80 °C under inert atmosphere for 24 h. After the mixture had cooled to room temperature, the solvent was removed under vacuum. The crude product was purified by column chromatography (silica gel) with petroleum ether/dichloromethane (50 to 100%) and then dichloromethane/methanol (0 to 2%) as eluent. Compound **2** was obtained as an orange solid (120 mg, 61% yield). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.79–2.04 (m, 60 H, alkyl chains), 4.02–4.09 (8 H, OCH_2), 7.14 (s, 2 H, H^{phen}), 7.22 (s, 2 H, H^{phen}), 7.33–7.46 (m, 4 H, H^{bpy}), 7.84–7.91 (m, 2 H, H^{bpy}), 8.14–8.27 (m, 6 H, H^{pyr}), 8.38–8.43 (m, 2 H, H^{bpy}), 8.57 (s, 3 H, H^{bpy}), 8.66–8.78 (m, 4 H, H^{bpy}), 8.84 (d, J = 9.1 Hz, 2 H, H^2 and H^7) ppm. MS (LSIMS$^+$), m/z: 1271 [M + 1]$^+$. Analysis calcd. (found) for $C_{88}H_{94}N_4O_4$ (1270): C 83.11 (82.01); H 7.45 (7.77); N 4.41 (3.56).

Acknowledgments

We are grateful to Dr. Jean Oberlé (Université Bordeaux 1, Talence, France) for his kind assistance in time-resolved fluorescence spectroscopy measurements.

[1] A. Laurent, *Ann. Chim. Phys.* **1837**, *66*, 136.
[2] E. S. Pysh, N. C. Yang, *J. Am. Chem. Soc.* **1963**, *85*, 2124.
[3] F. M. Winnik, *Chem. Rev.* **1993**, *93*, 587.
[4] K. Yamana, T. Iwai, Y. Ohtani, S. Sato, M. Namakura, H. Nakano, *Bioconjugate Chem.* **2002**, *13*, 1266, and references therein.
[5] J. Daub, M. Beck, A. Knorr, H. Spreitzer, *Pure Appl. Chem.* **1996**, *68*, 1399.
[6] R. B. Martin, L. Qu, B. A. Harruff, C. E. Bunker, J. R. Gord, L. F. Allard, Y.-P. Sun, *J. Phys. Chem. B* **2004**, *108*, 11447.
[7] a) J. Strauss, J. Daub, *Org. Lett.* **2002**, *4*, 683; b) A. C. Benniston, A. Harriman, D. J. Lawrie, A. Mayeux, K. Rafferty, O. D. Russel, *Dalton Trans.* **2003**, 4762.
[8] V. de Halleux, J.-P. Calbert, P. Brocorens, J. Cornil, J.-P. Declercq, J.-L. Brédas, Y. Geerts, *Adv. Funct. Mater.* **2004**, *14*, 649.
[9] M. Barboiu, L. Prodi, M. Montalti, N. Zaccheroni, N. Kyritsakas, J.-M. Lehn, *Chem. Eur. J.* **2004**, *10*, 2953.
[10] a) F. Fages, S. Leroy, T. Soujanya, J.-E. Sohna Sohna, *Pure Appl. Chem.* **2001**, *73*, 411; b) B. Bodenant, F. Fages, M.-H. Delville, *J. Am. Chem. Soc.* **1998**, *120*, 7511; c) J.-E. Sohna Sohna, V. Carrier, F. Fages, E. Amouyal, *Inorg. Chem.* **2001**, *40*, 6061.
[11] a) A. Harriman, M. Hissler, R. Ziessel, *Phys. Chem. Chem. Phys.* **1999**, *1*, 4203; b) B. Maubert, N. D. McClenaghan, M. T. Indelli, S. Campagna, *J. Phys. Chem. A* **2003**, *107*, 447.
[12] a) D. S. Tyson, K. B. Henbest, J. Bialecki, F. N. Castellano, *J. Phys. Chem. A* **2001**, *105*, 8154; b) A. F. Morales, G. Accorsi, N. Armaroli, F. Barigelletti, S. J. A. Pope, M. D. Ward, *Inorg. Chem.* **2002**, *41*, 6711.
[13] A. L. Rodriguez, G. Perron, C. Duprat, M. Vallier, E. Fouquet, F. Fages, *Tetrahedron Lett.* **1998**, *39*, 1179.
[14] T. Soujanya, A. Philippon, S. Leroy, M. Vallier, F. Fages, *J. Phys. Chem. A* **2000**, *104*, 9408.
[15] a) S. Leroy, T. Soujanya, F. Fages, *Tetrahedron Lett.* **2001**, *42*, 1665; b) S. Leroy-Lhez, A. Parker, P. Lapouyade, C. Belin, L. Ducasse, J. Oberlé, F. Fages, *Photochem. Photobiol. Sci.* **2004**, *3*, 949.
[16] S. Leroy-Lhez, C. Belin, A. D′Aléo, R. M. Williams, L. De Cola, F. Fages, *Supramol. Chem.* **2003**, *15*, 627.
[17] J. Roncali, *Acc. Chem. Res.* **2000**, *33*, 147.
[18] A. Del Guerzo, S. Leroy, F. Fages, R. H. Schmehl, *Inorg. Chem.* **2002**, *41*, 359.
[19] A. El-Ghayoury, R. Ziessel, *Tetrahedron Lett.* **1997**, *38*, 2471.
[20] a) C. G. Bangcuyo, M. E. Rampey-Vaughn, L. T. Quan, S. M. Angel, M. D. Smith, U. H. F. Bunz, *Macromolecules* **2002**, *35*, 1563, and references cited therein; b) K. D. Ley, Y. T. Li, J. V. Johnson, D. H. Powell, K. S. Schanze, *Chem. Commun.* **1999**, 1749; c) K. D. Ley, K. S. Schanze, *Coord. Chem. Rev.* **1998**, *171*, 287; d) B. Wang, M. R. Wasielewski, *J. Am. Chem. Soc.* **1997**, *119*, 12; e) M. Bouachrine, J.-P. Lère-Porte, J. J. E. Moreau, F. Serein-Spirau, C. Toreilles, *J. Mater. Chem.* **2000**, *10*, 263.
[21] R. G. Harvey, J. Pataki, H. Lee, *Org. Prep. Proced. Int.* **1984**, *16*, 3017.
[22] J. Grimshaw, J. Trocha-Grimshaw, *J. Chem. Soc., Perkin Trans. 1* **1972**, 1622.
[23] L. Chouai, F. Wu, Y. Jang, R. P. Thummel, *Eur. J. Inorg. Chem.* **2003**, 2774.
[24] H. Lee, R. G. Harvey, *J. Org. Chem.* **1986**, *51*, 2847.
[25] D. M. Connor, S. D. Allen, D. M. Collard, C. L. Liotta, D. A. Schiraldi, *J. Org. Chem.* **1999**, *64*, 6888.
[26] M. Kreyenschmidt, M. Baumgarten, N. Tyutyulkov, K. Müllen, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1957.
[27] T. M. Swager, C. J. Gil, M. S. Wrighton, *J. Phys. Chem.* **1995**, *99*, 4886–4893.
[28] V. K. Chaikovski, A. N. Novikov, *J. Org. Chem. USSR (Engl. Trans.)* **1984**, *20*, 1350–1352.

Received: January 25, 2005

