Synthesis and Spectroscopic Properties of Arene-Substituted Pyrene Derivatives as Model Compounds for Fluorescent Polarity Probes

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Keywords: Cross-coupling / Pyrene / Fluorescent polarity probes / Solvatochromism

In this paper, the syntheses of a variety of substituted phenyl pyrenes **5a**–**n** by Suzuki cross-coupling and of two decoupled analogues **10** and **17** are reported. These compounds have been investigated by fluorescence spectroscopy. The solvatochromism of their emission bands (Stokes shift) and the quantum yields in methylcyclohexane and acetonitrile have been determined. Furthermore, the crystal structure of a pyrenyl-tris(2,2′-bipyridine)ruthenium(II) complex **19** is presented.

Introduction

The ultimate goal of this long-term project is to synthesize spherical dendrimers,[1−5] in which photoinduced directed charge transfer[6−9] can take place from the interior to the exterior along the dendritic wedges. The intention is to create systems with a relatively long lifetime of the charge-separated photoexcited state to mimic charge-separation processes in biological photosystems.[10,11] If an electron donor is chosen as the core and the dendritic wedges are equipped with electron acceptors at defined positions (generations), several electron-transfer (ET) steps should be possible relaying the electron from acceptor to acceptor, akin to the multi-step ET involved in photosynthesis, provided that there is a free-energy gradient to provide the necessary driving force.[12−15] This gradient could be based on polarity. The first step is to clarify whether it is possible to generate and quantify a solvent-induced polarity gradient either by structural modifications[16] or by exploiting position-dependent solvation. If the density gradient of a dendrimer *decreases* on going from its interior to its exterior, as SANS measurements[17] and computational studies[18,19] have indicated for certain systems, local polarity created by the penetration of polar solvent molecules would be expected to *increase* in this direction.[20−22] This effect might be quantified by analyzing the fluorescence of site-specifically incorporated polarity probes based on solvatochromism.[23,24−28] In this project, acceptor-substituted pyrene derivatives that are covalently bound at specific generations of the dendrimer are employed as fluorescence probes.[29,30] Due to the bulkiness of the probes in comparison with the dendrimer skeleton, our concept involves so-called volume dummies, which are incorporated into those generations not bearing the probes in order to maintain the same steric and chemical microenvironment at each generation.[31]

Herein, we describe the synthesis of a series of 1-pyrenyl arenes as well as of two model compounds for use as volume dummies and report their spectroscopic properties in a homogeneous solvent environment. As yet, they do not bear functional groups for dendrimer synthesis but are supposed to serve as model compounds for the rational design of optimized fluorescent polarity probes and dummy building blocks to be used in the synthesis of the target dendrimers.[32]

Results and Discussion

Pyrene was chosen as the basic fluorophore because of its well-documented photochemistry[33] and the ready accessibility of suitable derivatives. Moreover, the fluorescence maxima of certain pyrene derivatives show large solvatochromic effects,[34−36] which is an important prerequisite for site-resolved probing of the local polarity in the interior of a dendrimer.

A series of pyrenes with the general structure **5** (Scheme 1) was prepared and the photoexcited-state properties were investigated in methylcyclohexane and acetonitrile. Compounds **5** consist of two parts, namely the pyrene donor and the substituted phenyl group in the 1-position, which serves as an electron acceptor; this renders the pyrene a highly polarity-sensitive probe. The electron acceptor bears electron-withdrawing groups of different strengths (R^1) (Table 1). The nature of the electron-withdrawing group was varied to ascertain which of them gave the largest solvatochromic effect. Additional substituents R^2 and R^3 in the *ortho*-positions of the phenyl ring can be expected to influence the phenyl/pyrenyl rotational barrier due to their steric demand and thus the accessibility of the charge-separated

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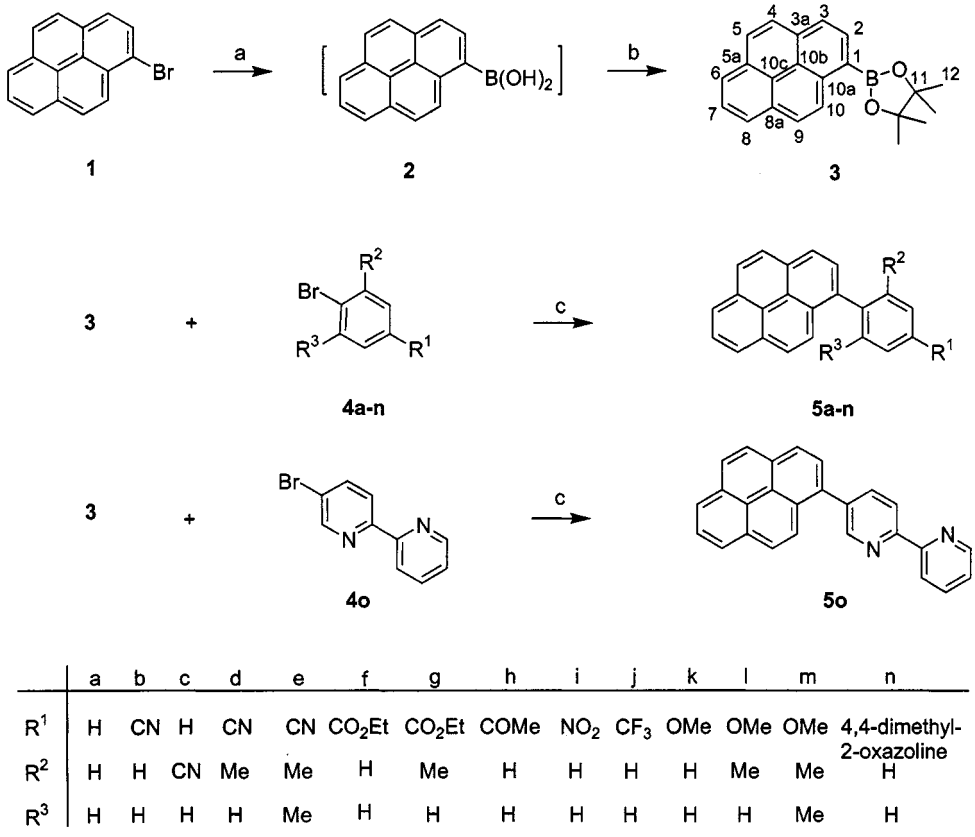


	a	b	c	d	e	f	g	h	i	j	k	l	m	n
R^1	H	CN	H	CN	CN	CO_2Et	CO_2Et	COMe	NO_2	CF_3	OMe	OMe	OMe	4,4-dimethyl-2-oxazoline
R^2	H	H	CN	Me	Me	H	Me	H	H	H	H	Me	Me	H
R^3	H	H	H	H	Me	H	H	H	H	H	H	H	Me	H

Scheme 1. (a) 1. *n*BuLi, Et_2O, −78 °C, 30 min, 2. $(iPrO)_3B$, −78 °C to room temp., 3. H^+/H_2O; (b) pinacol, 40 °C, 45 min; (c) $Pd(PPh_3)_4$, toluene, 1 M Na_2CO_3, reflux, 16−20 h

state (Table 1). A few examples with electron-donating substituents on the phenyl ring were also synthesized. Compounds **10** and **17** (Schemes 3 and 4) differ from **5b** only by a methylene and an ethylene spacer unit, respectively, between the donor and acceptor and were prepared and investigated as potential volume dummies.

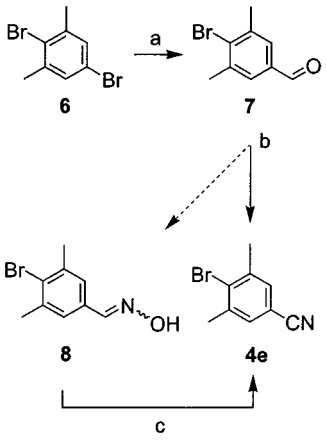
Synthesis

The most common procedure for aryl/aryl couplings at the 1-position of pyrenes is the Gomberg reaction of diazonium arenes with pyrene.[36−38] The products are formed in low yields (5 to 20%) and are accompanied by regioisomers. Suzuki cross-coupling (SCC),[39,40] as the presently most efficient and widely applicable aryl/aryl coupling reaction, was employed as the key reaction for the coupling of the donor and acceptor parts of **5**. There have only been two previous reports of the application of SCC to this synthesis.[41,42]

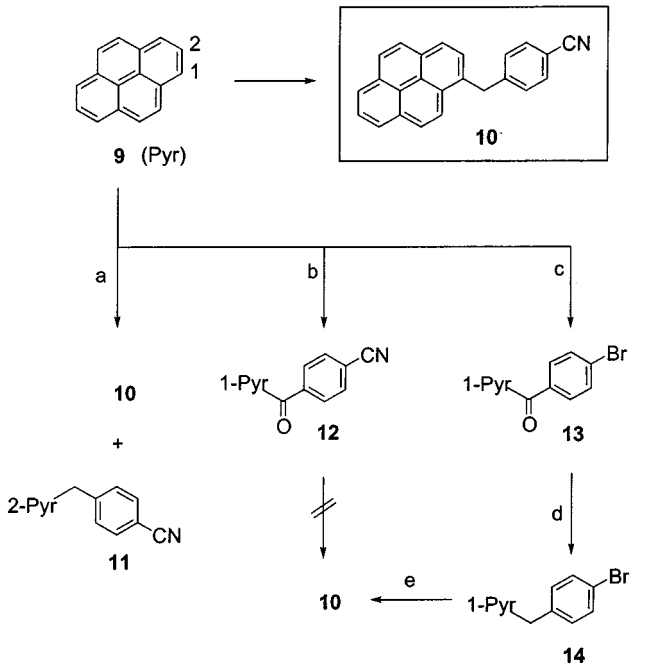
Borylation of the commercially available 1-bromopyrene **1** and subsequent esterification of the crude free boronic acid **2** with pinacol gave the boronic ester **3** in 80% yield based on **1** (Scheme 1). Compound **3** was prepared on a 25 g scale. The intermediate free acid **2**[41−45] was not usually isolated due to its low solubility, but it was characterized by NMR spectroscopy and mass spectrometry. All signals in the ^1H and ^{13}C NMR spectra of **3** could be unambiguously assigned by applying heteronuclear multiple quantum correlation (HMQC) NMR. The 2-H and 10-H protons absorb at $\delta = 8.7$ and 9.2, respectively, which is remarkably downfield shifted and typical of aryl protons in the vicinity of a boronic ester function. The pinacol ester **3** can be stored for months on the laboratory bench without any change, as verified by HPLC.

With the exception of **4e**,[46] the bromoarenes **4a**−**o** used for the coupling reactions with **3** were either purchased (**4a**−**d**, **4f**, **4h**−**k**) or were prepared according to literature procedures. Compound **4e** was synthesized according to the sequence shown in Scheme 2. The product of the regioselective lithiation of the dibromoxylene **6** at C-5[47] with butyllithium in diethyl ether at −78 °C was formylated with dimethylformamide (DMF)[48] to produce the benzaldehyde **7**. Reaction of **7** with hydroxylamine and subsequent thermally induced dehydration gave benzonitrile **4e** in 39% yield.[49] Accompanying amounts of non-dehydrated oxime **8** were removed by column chromatography and identified by NMR spectroscopy and mass spectrometry. The yield of **4e** could be increased to 81% by dehydration of **8** to **4e** with carbon disulfide in the presence of aqueous sodium hydroxide.[50]

SCC reactions yielding **5a**−**o** (Scheme 1) were carried out under standard conditions using an equimolar ratio of the substrates in a heterogeneous solvent system of toluene and 1 M aq. Na_2CO_3 using 2 mol % $Pd(PPh_3)_4$ as the catalyst precursor. The yields and selected spectroscopic data of



Scheme 2. (a) 1. *n*BuLi, Et_2O, −78 °C, 30 min, 2. DMF; (b) hydroxylamine hydrochloride, pyridine, toluene, reflux, 2 h; (c) CS_2, 3 M NaOH, $(nBu)_4NHSO_4$, room temp., 20 h



Scheme 3. (a) 4-(Bromomethyl)benzonitrile, $AlCl_3$, CS_2; (b) 4-cyanobenzoyl chloride, $AlCl_3$, CS_2, reflux; (c) 4-bromobenzoyl chloride, $AlCl_3$, CS_2, reflux; (d) $NaBH_4$, $AlCl_3$, THF, reflux, 90 min; (e) CuCN, DMF, reflux

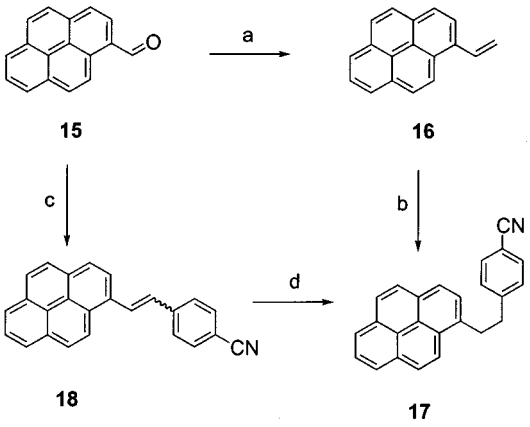
compounds **5a**−**o** are summarized in Table 1. The coupling is sensitive to the substituents R^2 and R^3 of **4**. The greater the steric demand, the lower the yield. In the case of the cyano-substituted arenes **5b**,**d**,**e**, the isolated yields decrease from 87% (**5b**) for the unsubstituted *para*-benzonitrile derivative to 53% (**5d**) in the presence of one methyl group in the position *ortho* to the bromo function, and decrease further to 28% (**5e**) with a second *ortho*-methyl group. The bulkiness of the pyrene moiety is considered as a possible explanation.[51]

Since benzonitrile **5b** was found to be a suitable polarity probe (see next section), two potential volume dummies **10** and **17** were synthesized that also bear the nitrile function but differ from **5b** by a methylene or ethylene bridge inserted between the donor and acceptor (Scheme 3 and Scheme 4). Friedel−Crafts alkylation of pyrene **9** with *p*-(bromomethyl)benzonitrile gave a mixture of the regioisomers **10** and **11** in low yield (Scheme 3), from which **10** could be obtained in analytically pure form. This route was nevertheless considered unsatisfactory because of the tedi-

Table 1. Chemical yields, UV absorption, and fluorescence data for the pyrenyl arene derivatives **5a**−**o** in methylcyclohexane (MCH) and acetonitrile (AN)

No.[a]	R^1	R^2	R^3	yield[b] (%)	λ_{abs} [nm][c] MCH	AN	λ_{fl} [nm] MCH	AN	$\Delta\nu_{St}$ [cm^{-1}][d] MCH	AN	$\Delta\gamma\Delta\nu_{St}$ [cm^{-1}]	Φ_{fl}[e] MCH	AN
5a	H	H	H	83	342	342	380, 400	381, 398	3599	3566	−33	0.41	0.58
5b	CN	H	H	87	343	344	391, 406	427	4060	5651	1591	0.69	0.81
5c	H	H	CN	66	343	342	383, 401	407	3644	4670	1026	0.21	0.34
5d	CN	Me	H	53	342	342	381, 388	401	3232	4302	1070	0.08	0.29
5e	CN	Me	Me	28	342	342	378, 389	378, 389	3467	3467	0	0.042	0.072
5f	CO_2Et	H	H	88	342	342	390, 404	424	4051	5655	1604	0.49	0.76
5g	CO_2Et	Me	H	46	342	342	388, 397	399	3096	4177	1081	0.07	0.24
5h	COMe	H	H	87	343	343	425	461	5625	7462	1837	0.011[f][g]	0.58[g]
5i	NO_2	H	H	78	342, 356[h]	340, 357[h]	392, 408	429	3090	4701	1611	0.006	0.002
5j	CF_3	H	H	85	342	342	387, 401	389, 402	3859	3955	96	0.11	0.21
5k	OMe	H	H	89	342	342	383, 403	387, 404	3794	3955	161	0.17	0.32
5l	OMe	Me	H	58	342	342	379, 399	380, 399	3533	3566	33	0.09	0.14
5m	OMe	Me	Me	37	343	344	381, 401	383, 402	3579	3592	13	0.14	0.20
5n	[i]	H	H	83	343	343	394	411	3774	4824	1050	0.38	0.66
5o	see Scheme 1[j]			78	344	344	406	436	4440	6137	1697	–	–

[a] Purity of all compounds ≥ 99.5% according to HPLC analysis. – [b] Yields were not optimized. – [c] Only the long-wavelength absorption maxima are given. – [d] Stokes shifts ($\Delta\nu_{St}$) have been calculated from the maxima of absorption and fluorescence (the mean value is taken in case of a vibrational structure). – [e] Fluorescence quantum yield. – [f] In hexane. – [g] Ref.[17c] – [h] Shoulder. – [i] 4,4-Dimethyl-2-oxazoline. – [j] Spectroscopic data of the corresponding Ru^{2+} complex **19**: λ_{abs} = 340 and 455 nm, λ_{fl} = 642 nm in tetrahydrofuran.



Scheme 4. (a) 1. Methyl triphenylphosphonium iodide, THF, 0 °C, 2. *n*BuLi, 3. **15**; (b) 1. 9-BBN, THF, room temp., 8 h, 2. 4-bromobenzonitrile, $Pd(PPh_3)_4$, 1 M Na_2CO_3, reflux, 16 h; (c) 1. (4-cyanobenzyl)triphenylphosphonium bromide, KO*t*Bu, THF, room temp., 30 min, 2. **15**, room temp., 2 h, then reflux, 20 h; (d) Mg, Pd/C, *n*-propanol, reflux, 24 h

ous recrystallization procedure required. An attempt to obtain **10** by reduction of the Friedel–Crafts acylation product **12** was unsuccessful. Only the corresponding alcohol (not shown) was obtained. Even though the employed conditions (Wolff–Kishner and $NaBH_4/AlCl_3$[52]) have been reported to have proved successful in similar cases, the strong electron-withdrawing effect of the cyano group may hinder the reduction.[53] Finally, **10** was synthesized in an overall yield of 40% by Friedel–Crafts acylation of the pyrene **9** with *para*-bromobenzoic acid chloride, reduction of the resulting ketone **13**[54] with $NaBH_4/AlCl_3$, and Rosenmund–von Braun cyanodehalogenation of **14** with CuCN in DMF.[55,56]

The ethylene-bridged homologue **17** could be obtained by two different methods (Scheme 4): (a) Hydroboration of 1-vinylpyrene **16**[57,58] with 9-borabicyclo[3.3.1]nonane (9-BBN) and subsequent Suzuki–Miyaura coupling[59,60] with *para*-bromobenzonitrile gave **17** in moderate yield; (b) Wittig reaction of pyrene aldehyde **15** with the phosphonium ylide of *para*-(bromomethyl)benzonitrile in the presence of KO*t*Bu in tetrahydrofuran gave the stilbene derivative **18** in 92% yield. Its hydrogenation to **17** proceeded quantitatively, as determined by HPLC. However, in practice, the yield is reduced by the work-up procedure. Method (b) turned out to be superior. It avoids the handling of 1-vinylpyrene with its propensity to polymerize and allows scale-up to 25 g of **17**.

Bichromic pyrene–ruthenium(II)–tris(2,2′-bipyridine) dyads have attracted some interest in recent years.[61,62] Some of these complexes show outstanding photophysical properties such as reverse triplet-triplet energy-transfer between the two partners. $Ru(bipy)_3^{2+}$ dyads with either one 1-pyrenyl moiety at the 4-position of one bipy[61] or with one 1-ethynylpyrenyl moiety at the 5-position of a bipy have been investigated in detail.[62] To contribute to this field we additionally applied our coupling method to the synthesis of 5-(pyren-1-yl)-2,2′-bipyridine (**5o**) (Scheme 1 and Table 1), the subsequent complexation of which with *rac*-

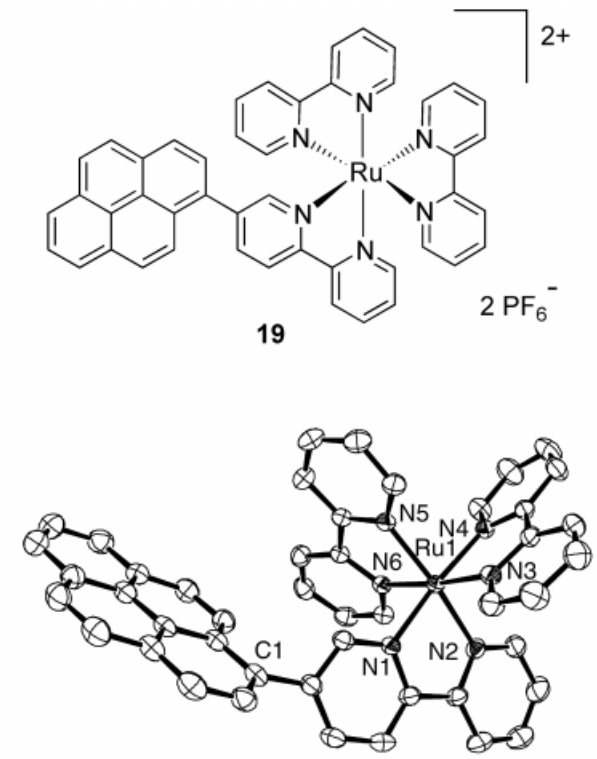


Figure 1. Structure and ORTEP[64] plot of the Λ-enantiomer of **19**

$Ru^{II}(bipy)_2Cl_2$ yielded *rac*-[bis(2,2′-bipyridine){5-(pyren-1-yl)-2,2′-bipyridine}ruthenium(II)] bis(hexafluorophosphate) (**19**) in 83% yield (Figure 1). Suitable crystals of **19** were obtained by slow diffusion of methanol into a dichloromethane solution. The X-ray structural analysis[63] was carried out at 153 K and revealed that **19** crystallizes with three molecules of dichloromethane per formula unit. Both enantiomeric Δ- and Λ-isomers were found in the unit cell (Figure 1).

UV Absorption and Fluorescence Measurements

The normalized absorption and fluorescence spectra of some of the pyrenyl arenes are depicted in Figure 2. The spectroscopic data are summarized in Table 1. The absorption spectra of all compounds show a single intense band with a maximum at around 340 nm and log ε values of about 4.5. They resemble those of the parent phenyl pyrene chromophore **5a**, except that of **5i**, which shows multiple absorption bands and a red shift. The negligible solvatochromic shift of the absorption spectra with the solvent polarity is consistent with a small difference between the dipole moments of the Franck–Condon (FC) excited state and the ground state and suggests a negligible degree of CT in the FC excited state, except in the case of **5i**. In general, the long-wavelength absorption band of the pyrenyl arenes corresponds to the $S_0–S_1$ (π,π*) transition. In the case of the nitro derivative **5i**, the involvement of a low-lying

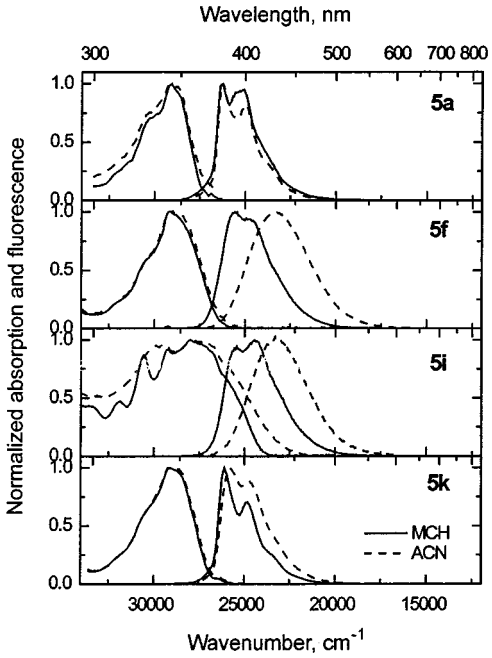


Figure 2. UV absorption and fluorescence spectra of **5a**, **5i**, **5f**, and **5k** in methylcyclohexane (MCH) and acetonitrile (AN)

charge-transfer absorption band may be invoked to explain the low-energy transition extending beyond 400 nm.

The fluorescence spectra in non-polar solvents such as methylcyclohexane show a maximum between 380 and 400 nm (Table 1). They are similar in appearance and in the position of the maximum to that of phenylpyrene **5a** (Figure 2). The fluorescence spectra are structured in methylcyclohexane but lose their vibrational structure in acetonitrile in the case of acceptor-substituted pyrenyl arenes. Solvatochromic measurements were carried out in order to investigate the change in the charge distribution between the FC and the equilibrated S_1 states. The difference between the energies of the absorption and fluorescence maxima is given by the Stokes shifts (Table 1). With the exception of those of **5a**, **5j**, and **5k**−**5m**, the fluorescence spectra are strongly red-shifted in the polar solvent acetonitrile, i.e. a strong solvatochromic effect is observed with increasing solvent polarity. It is deduced from these observations that by introducing an acceptor substituent on the phenyl group a substantial charge transfer takes place after excitation and geometrical relaxation of the molecules on the excited-state surface.

For all the compounds (**5c**−**5e**, **5g**, **5l**, **5m**) for which the ground-state dihedral angle between the pyrene and the phenyl moiety is increased by the introduction of *ortho* substituents at the phenyl group, a decrease in the Stokes shifts is observed with respect to the unhindered compound. Therefore, it can be assumed that the pyrenyl arenes undergo a flattening in the excited state and that the charge-transfer state is stabilized by mesomeric interactions.

From the data presented here, no clear conclusion can be drawn regarding the nature of the relaxation coordinate on the excited-state surface, especially for the sterically hindered compounds. However, the fluorescent charge-transfer states in acetonitrile can be rationalized in terms of a mixing of ^1L_b and/or ^1L_a with ET states in various proportions. A detailed mechanistic study regarding the properties of the photoexcited state and the kinetics of the relaxation pathway is under investigation.

The quantum yield of the fluorescence is another important parameter in examining the ability of pyrenyl arenes to act as fluorescent probes (Table 1). Moderate to high values (0.1−0.8) have been determined for most of the pyrenyl arenes, with larger values being recorded in acetonitrile than in methylcyclohexane. The low values (< 0.1) measured for **5d**, **5g**, and **5l** in methylcyclohexane and for **5e**, **5i** in both solvents indicate a significant involvement of non-radiative relaxation pathways.

In the dendrimers, the polarity probes will be applied in combination with structurally related volume dummies to maintain the overall structure of the dendrimers. The requirement that the volume dummies should not absorb light at the wavelengths at which the probe molecules are excited can be achieved by decoupling the π-electron systems of the pyrene and arene moieties by introducing a methylene or ethylene bridge between the two groups. An example of a suitable combination of a polarity probe and volume dummy is given by **5b** and (4-cyanobenzyl)pyrene (**10**). Their UV absorption and fluorescence spectra (Figure 3) indicate that for wavelengths > 360 nm a selective excitation of the probe, irrespective of the solvent polarity, should be possible. Corresponding results were obtained for the ethylene-bridged derivative **17**.

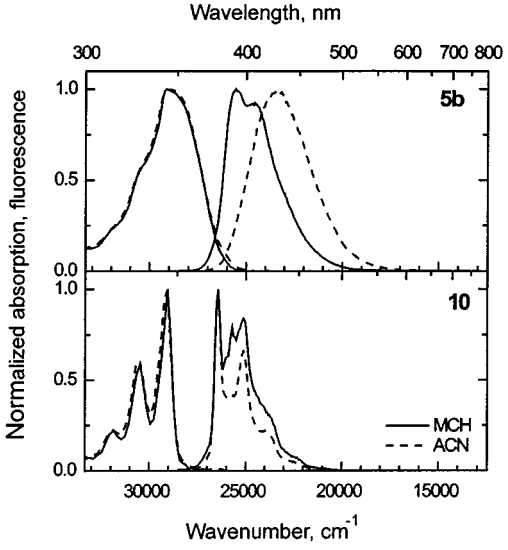


Figure 3. Comparison of the UV absorption and fluorescence spectra of the cyano-functionalized polarity probe **5b** and the corresponding volume dummy **10** in methylcyclohexane (MCH) and acetonitrile (AN)

In the dendrimers, the UV and fluorescence spectra of the probes and dummies will be superimposed. The ratio of the number of probe molecules to the dummy chromophores depends on the number of generations and the structure of the dendrimer. With increasing number of genera-

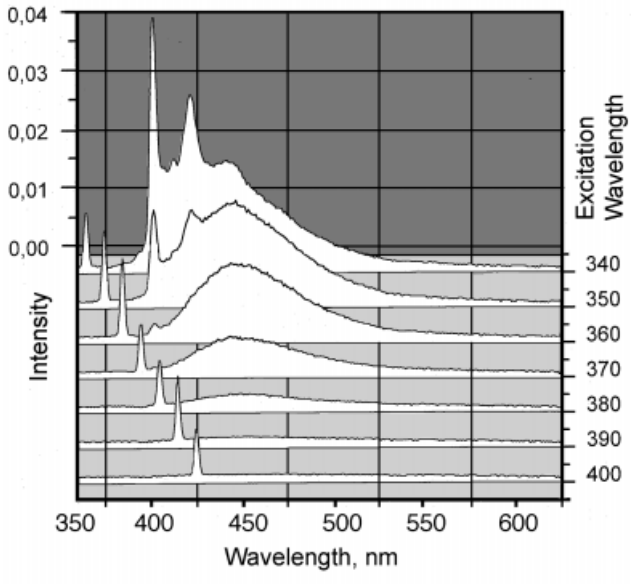


Figure 4. Excitation wavelength dependence of the fluorescence spectra of a 1:14 mixture of **5b** and **10** in acetonitrile, which represents a realistic ratio in a G4 dendron with the probe introduced in the first generation; selective excitation of the probe is seen at $\lambda_{exc} > 360$ nm

tions this ratio will decrease, i.e. the number of the probes will be considerably smaller than the number of volume dummies. Figure 4 shows the fluorescence spectra of a mixture of both components in a concentration ratio of 1:14 (**5b/10**) to simulate a dendrimer of the fourth generation. The fluorescence spectra were recorded with reference to the excitation wavelength. The spectrum recorded at $\lambda_{exc} =$ 340 nm displays the fluorescence maxima of both the probe and the dummy, whereas the spectra recorded at $\lambda_{exc} >$ 360 nm show exclusively the fluorescence spectrum of the probe.

Conclusion

A variety of acceptor- and donor-substituted pyrene derivatives have been synthesized using SCC as the key reaction step. Investigation of their excited states in solvents of different polarity has shown that, due to the combination of a moderately strong solvatochromism and a high fluorescence quantum yield, the cyano and ester derivatives **5b** and **5f**, respectively, should be especially suitable as fluorescent probes to report the polarity of the surrounding medium. Likewise, the volume dummies, i.e. the decoupled derivatives **10** and **17** for the cyano series, should serve their proposed function.

For future probe design, the introduction of additional acceptor groups on the phenyl ring is envisaged as allowing further improvement of the properties of these polarity probes based on solvatochromism caused by charge transfer in the excited state.

Experimental Section

General: All chemicals for synthesis were purchased from Aldrich or Acros Chimica and were used without further purification. Several compounds were prepared according to literature procedures and gave satisfactory NMR and MS data: **4g**,[65] **4l**,[66] **4m**,[67,68] **4n**,[69] **4o**,[70,71] **6**,[47] **13**,[54] **15**,[72] **16**,[57] (4-cyanobenzyl)triphenylphosphonium bromide.[73] $Pd(PPh_3)_4$ was prepared according to ref.[74] and was used without further characterization. Compounds **5a**,[75,76] **5h**,[36] **5i**,[37] **13**,[54] and **18**[73] are included in the Experimental Section in view of the lack of spectroscopic data in the literature. All other compounds are new (CAS-online January 2000). Diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone ketyl or potassium/benzophenone ketyl; the toluene used was of p.a. quality. All cross-coupling reactions were carried out under oxygen-free conditions. − Melting points: Büchi SMP 510 (open capillaries, uncorrected values). − NMR: Bruker AC 250, AM 270, AMX 500 (^{1}H: $CDCl_3$ at $\delta = 7.24$, ^{13}C: $CDCl_3$ at $\delta = 77.0$ as internal standards, 20 °C). − MS: Perkin−Elmer Varian MAT 711, electron-impact (EI) mode. − IR: Nicolet 5SXC (FT-IR). − Elemental analyses: Perkin−Elmer EA 240. − Column chromatography: Merck silica gel 60, 0.040−0.063 mm (230−400 mesh). − RP-HPLC: Macherey-Nagel, Nucleosil® 7μm C_{18}, UV detection at 335 nm.

Spectrophotometric grade methylcyclohexane and acetonitrile were used as solvents for the spectroscopic measurements. For the fluorescence measurements, the pyrenyl derivatives **5a**−**o**, **10**, and **17** were purified by preparative HPLC to ensure purities of > 99.5%. UV absorption spectra were measured on an ATI UNICAM UV series UV-02113 spectrometer; fluorescence spectra were recorded on an AMINCO-Bowman series 2 spectrofluorimeter. They were corrected for instrumental sensitivity. A solution of quinine bisulfate in 0.1 N H_2SO_4 ($\Phi_f = 0.52$)[77] was employed as a standard for the measurement of the fluorescence quantum yields.

4,4,5,5-Tetramethyl-2-pyren-1-yl-1,3,2-dioxaborolane (3): *n*-butyllithium (2.6 mL of a 1.6 M solution in hexane, 4.16 mmol, 1.09 equiv.) was added dropwise. To a solution of 1-bromopyrene (1.07 g, 3.81 mmol) in tetrahydrofuran (50 mL) at −78 °C. After stirring for 30 min at this temperature, triisopropyl borate (1.75 mL, 7.58 mmol, 2.00 equiv.) was added and the solution was allowed to warm to room temperature over a period of 30 min. Then, 5% hydrochloric acid (50 mL) was added, the layers were separated, and the aqueous phase was extracted with diethyl ether (3 ×). The combined organic phases were treated with 2,3-dimethyl-2,3-butanediol (pinacol) (1.46 g, 12.35 mmol, 3.24 equiv.) and the solution was stirred at 40 °C for 45 min until the reaction was complete, as indicated by the disappearance of the free boronic acid upon TLC analysis. After removal of the solvent in vacuo, the remaining dark oil was chromatographed on silica gel (hexane/ethyl acetate, 20:1). Precipitation from dichloromethane/methanol gave 1.06 g (85%) of **3** as a yellowish solid; m.p. 123 °C. − $R_f = 0.24$ (hexane/ethyl acetate, 20:1). − ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.55$ (s, 12 H, 12-H), 8.04 (t, $^3J = 7.6$ Hz, 1 H, 7-H), 8.09 (d, $^3J = 8.8$ Hz, 1 H, 4-H), 8.13 (d, $^3J = 8.8$ Hz, 1 H, 5-H), 8.21 (d, $^3J = 7.6$ Hz, 1 H, 6-H), 8.23 (d, $^3J = 9.0$ Hz, 1 H, 9-H), 8.24 (d, $^3J = 7.6$ Hz, 1 H, 3-H), 8.26 (d, $^3J = 7.6$ Hz, 1 H, 8-H), 8.67 (d, $^3J = 7.6$ Hz, 1 H, 2-H), 9.21 (d, $^3J = 9.0$ Hz, 1 H, 10-H). − ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 25.0$ (C-12), 83.8 (C-11), 124.0 (C-3), 124.3 (C-10b), 124.5 (C-10c), 125.1 (C-6), 125.3 (C-8), 125.6 (C-7), 127.4 (C-4), 127.7 (C-9), 128.0 (C-10), 128.5 (C-5), 130.7 (C-8a), 131.0 (C-5a), 133.4 (C-3a), 133.8 (C-2), 136.4 (C-10a). − MS (70 eV, 135°C): *m/z* (%) = 328 (100) $[M]^+$, 313 (1), 270 (5), 255 (13), 228

(56), 202 (7). − IR (KBr): $\tilde{\nu}$ = 3046 (w), 2970 (m), 2926 (w), 1347, 1355, 1371, 1378, 1388 cm^{-1} [s, Ar−B(OH)$_2$]. − $C_{22}H_{21}BO_2$ (328.21): calcd. C 80.51, H 6.45; found C 80.42, H 6.31.

Pyren-1-ylboronic Acid (2): This compound was obtained by chromatographic separation (hexane/ethyl acetate, 20:1, then ethanol) of the crude product after extractive work-up as described for **3**, followed by precipitation from ethanol; m.p. > 265 °C. − ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 8.04 (t, ^3J = 7.5 Hz, 1 H, 7-H), 8.14−8.30 (m, 6 H), 8.35 (d, ^3J = 7.5 Hz, 1 H, 2-H), 8.66 [s, 2 H, B(OH)$_2$], 8.79 (d, ^3J = 9.0 Hz, 1 H, 10-H). − ^{13}C NMR (63 MHz, [D$_6$]DMSO): δ = 123.1, 123.7, 124.1 (br), 125.0 (br), 126.0 (br), 126.9 (br), 127.6 (br), 128.6 (br), 130.5, 130.9, 131.5, 131.9 (br), 132.6 (br), 134.1. − MS (70 eV, 40 °C): *m*/*z* (%) = 246 (33) [M]$^+$, 228 (21) [M − H$_2$O]$^+$, 202 (18) [M − B(OH)$_2$]$^+$. − HRMS: *m*/*z* calcd. for $C_{16}H_{11}BO_2$ 246.08521; found 246.08921.

4-Bromo-3,5-dimethylbenzaldehyde (7): A solution of 2,5-dibromoxylene **6** (1.90 g, 7.20 mmol) in diethyl ether (20 mL) was treated with *n*-butyllithium (4.5 mL of a 1.6 M solution in hexane, 1.0 equiv.) at −78 °C. After stirring for 45 min, *N*,*N*-dimethylformamide (1.7 mL, 22.0 mmol, 3.06 equiv.) was added and the solution was allowed to warm to room temperature. It was then acidified with 5% hydrochloric acid and extracted with diethyl ether. The residue obtained after standard work-up was chromatographed on silica gel (hexane/ethyl acetate, 10:1) and crystallized from diethyl ether to give 1.21 g (79%) of **7** as colorless crystals; m.p. 67 °C. − R_f = 0.49 (hexane/ethyl acetate, 6:1). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.46 (s, 6 H), 7.54 (s, 2 H), 9.91 (s, 1 H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 23.8, 128.8, 132.5, 134.8, 139.5, 191.6. − MS (80 eV, 30 °C): *m*/*z* (%) = 214 (80) [$C_9H_9{}^{81}BrO$]$^+$, 212 (78) [$C_9H_9{}^{79}BrO$]$^+$, 211 (100) [$C_9H_8{}^{79}BrO$]$^+$. − IR (KBr): $\tilde{\nu}$ = 1684 cm^{-1} (CO, vs). − C_9H_9BrO (213.07): calcd. C 50.73, H 4.26; found C 50.51, H 4.35.

4-Bromo-3,5-dimethylbenzonitrile (4e). − (I) From Benzaldehyde 7: Aldehyde **7** (1.05 g, 4.93 mmol) was dissolved in a mixture of hydroxylamine hydrochloride (0.37 g, 5.33 mmol, 1.08 equiv.) and pyridine (0.81 mL, 10.02 mmol, 2.03 equiv.). After a few minutes, toluene (5 mL) was added and the solution was heated under reflux for 2 h in an apparatus fitted with a water trap. The reaction mixture was subsequently extracted with toluene (3 ×), the combined organic phases were dried with $MgSO_4$, and the solvent was evaporated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate, 10:1). Yield: 39% of **4e**. The main product was 4-bromo-3,5-dimethylbenzaldehyde oxime **8** (see below); m.p. 144 °C. − R_f = 0.48 (hexane/ethyl acetate, 6:1). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.43 (s, 6 H), 7.32 (s, 2 H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 3.7, 110.6, 118.3, 131.0, 133.1, 139.9. − MS (80 eV, 40 °C): *m*/*z* (%) = 211 (99) [$C_9H_8{}^{81}BrN$]$^+$, 209 (100) [$C_9H_8{}^{79}BrN$]$^+$. − IR (KBr): $\tilde{\nu}$ = 2222 cm^{-1} (CN, m). − C_9H_8BrN (210.07): calcd. C 51.46, H 3.84, N 6.67; found C 51.11, H 3.68, N 6.59.

4-Bromo-3,5-dimethylbenzaldehyde Oxime (8): The aldoxime **8** was isolated as the main product in the synthesis of **4c** according to route **I** in 56% yield. − R_f = 0.20 (hexane/ethyl acetate, 6:1). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.41 (s, 6 H), 7.26 (s, 2 H), 8.04 (s, 1 H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 23.8, 126.5, 129.5, 130.3, 138.9, 149.7. − MS (80 eV, 50 °C): *m*/*z* (%) = 229 (98) [$C_9H_{10}{}^{81}BrNO$]$^+$, 227 (100) [$C_9H_{10}{}^{79}BrNO$]$^+$. − $C_9H_{10}BrNO$ (228.09).

4-Bromo-3,5-dimethylbenzonitrile (4e). − (II) From Benzaldehyde Oxime (8): Aldoxime **8** (0.40 g, 1.76 mmol) was suspended in a mixture of carbon disulfide (0.75 mL), aqueous sodium hydroxide solution (3 M, 1 mL), toluene (3 mL), and tetra-*n*-butylammonium hydrogen sulfate (0.14 g, 0.41 mmol). The mixture was stirred for 20 h at room temperature. After extractive work-up with toluene, the residue was chromatographed on silica gel (hexane/ethyl acetate, 10:1). The product was precipitated from dichloromethane/methanol to give 0.30 g (75%) of the benzonitrile **4e** as colorless crystals.

Typical Procedure for the Suzuki Cross-Coupling of 3 and 4a−o

3,5-Dimethyl-4-pyren-1-yl-benzonitrile (5e): After degassing a mixture of **3** (0.36 g, 1.10 mmol), **4e** (0.23 g, 1.09 mmol), toluene (20 mL), and aqueous sodium hydroxide solution (1 M, 10 mL), the catalyst precursor Pd(PPh$_3$)$_4$ (25.4 mg, 2 mol%) was added and the mixture was stirred under reflux for 20 h. The layers were then separated, the aqueous phase was extracted with toluene (3 ×), the combined organic phases were dried with $MgSO_4$, and the solvent was evaporated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate, 20:1) to give 0.10 g (28%) of **5e**; m.p. 217−218 °C. − R_f = 0.23 (hexane/ethyl acetate, 20:1). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.92 (s, 6 H), 7.45 (d, ^3J = 9.0 Hz, 1 H), 7.53 (s, 1 H), 7.71 (d, ^3J = 7.5 Hz, 1 H), 7.98 (d, ^3J = 9.0 Hz, 1 H), 8.03 (d, ^3J = 7.5 Hz, 1 H), 8.13 (s, 1 H), 8.18 (d, ^3J = 7.5 Hz, 1 H), 8.23 (d, ^3J = 7.5 Hz, 1 H), 8.27 (d, ^3J = 7.5 Hz, 1 H). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.5, 111.2, 119.3, 123.8, 124.7, 124.9, 125.1, 125.3, 125.5, 126.0, 126.2, 127.3, 127.7, 128.1, 128.2, 130.8, 130.9, 131.2, 134.0, 138.8, 145.4. − MS (80 eV, 120 °C): *m*/*z* (%) = 331 (100) [M]$^+$, 314 (37), 301 (11), 202 (4). − $C_{25}H_{17}N$ (331.41): calcd. C 90.60, H 5.17, N 4.23; found C 90.19, H 5.18, N 4.27.

1-Phenylpyrene (5a): M.p. 93 °C. − R_f = 0.26 (hexane). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.51−7.72 (m, 5 H), 7.99−8.27 (m, 9 H). − ^{13}C NMR (126 MHz, $CDCl_3$): δ = 124.6, 124.78, 124.84, 124.9, 125.1, 125.2, 126.0, 127.2, 127.4, 127.4, 127.6, 128.3, 128.4, 130.5, 130.6, 130.9, 131.4, 137.7, 141.2. − MS (70 eV, 110 °C): *m*/*z* (%) = 278 (100) [M]$^+$. − $C_{22}H_{14}$ (278.35): calcd. C 94.93, H 5.07; found C 94.48, H 5.02.

4-(Pyren-1-yl)benzonitrile (5b): M.p. 153 °C. − R_f = 0.10 (hexane/ethyl acetate, 20:1). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.68 (d, ^3J = 8.5 Hz, 2 H), 7.81 (d, ^3J = 8.5 Hz, 2 H), 7.88 (d, ^3J = 7.8 Hz, 1 H), 7.99−8.23 (m, 8 H). − ^{13}C NMR (126 MHz, $CDCl_3$): δ = 110.9, 118.9, 124.1, 124.6, 125.5, 126.2, 127.0, 127.2, 128.0, 128.1, 130.7, 131.1, 131.3, 132.0, 135.2, 146. 0. − MS (70 eV, 315 °C): *m*/*z* (%) = 303 (100) [M]$^+$, 276 (4), 138 (6). − IR (KBr): $\tilde{\nu}$ = 2224 cm^{-1} (CN, m). − $C_{23}H_{13}N$ (303.36): calcd. C 91.06, H 4.32, N 4.62; found C 91.11, H 4.59, N 4.53.

2-(Pyren-1-yl)benzonitrile (5c): M.p. 176 °C. − R_f = 0.10 (hexane/ethyl acetate, 20:1). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.55 (t, ^3J = 7.5 Hz, 1 H), 7.63 (d, ^3J = 7.5 Hz, 1 H), 7.72 (t, ^3J = 7.5 Hz, 1 H), 7.81 (d, ^3J = 10.0 Hz, 1 H), 7.89 (d, ^3J = 7.5 Hz, 1 H), 7.97 (m, 3 H), 8.12 (s, 2 H), 8.18 (d, ^3J = 7.5 Hz, 1 H), 8.22 (d, ^3J = 7.5 Hz, 1 H), 8.26 (d, ^3J = 8.0 Hz, 1 H). − ^{13}C NMR (126 MHz, $CDCl_3$): δ = 113.8, 118.2, 124.2, 124.55, 124.59, 124.8, 125.3, 125.6, 126.2, 127.3, 127.4, 127.9, 128.1, 128.2, 128.8, 130.7, 131.3, 131.6, 132.0, 132.3, 133.0, 133.2, 144.8. − MS (70 eV, 120 °C): *m*/*z* (%) = 303 (100) [M]$^+$, 276 (6), 138 (7). − IR (KBr): $\tilde{\nu}$ = 2218 cm^{-1} (CN, m). − HRMS: *m*/*z* calcd. for $C_{23}H_{13}N$ 303.10480; found 303.10623.

3-Methyl-4-(pyren-1-yl)benzonitrile (5d): M.p. 176 °C. − R_f = 0.10 (hexane/ethyl acetate, 20:1). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.06 (s, 3 H), 7.45 (d, ^3J = 7.5 Hz, 1 H), 7.57 (d, ^3J = 10.0 Hz, 1 H), 7.64 (d, ^3J = 8.5 Hz, 1 H), 7.68 (s, 1 H), 7.79 (d, ^3J = 7.5 Hz,

1 H), 8.02 (dd, ^3J = 8.5 Hz, 2 H), 8.12 (s, 2 H), 8.18 (d, ^3J = 7.5 Hz, 1 H), 8.23 (d, ^3J = 8.5 Hz, 2 H). − ^{13}C NMR (126 MHz, $CDCl_3$): δ = 20.1, 111.5, 119.1, 124.4, 124.58, 124.63, 125.3, 125.5, 126.2, 126.5, 127.3, 127.8, 128.1, 128.4, 129.4, 130.8, 131.0, 131.3, 131.5, 133.4, 134.9, 138.6, 145.8. − MS (80 eV, 160 °C): *m/z* (%) = 317 (100) $[M]^+$. − IR (KBr): ṽ = 2230 cm^{-1} (CN, s). − $C_{24}H_{15}N$ (317.38): calcd. C 90.82, H 4.76, N 4.41; found C 90.77, H 4.86, N 4.23.

Ethyl 4-(Pyren-1-yl)benzoate (5f): M.p. 129 °C. − R_f = 0.44 (hexane/ethyl acetate, 6:1). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.37 (t, 3 H), 4.39 (q, 4 H), 7.57 (d, ^3J = 8.0 Hz, 2 H), 7.80−8.17 (m, 11 H). − ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.4, 61.1, 124.6, 124.8, 124.9, 125.0, 125.8, 126.1, 127.31, 127.34, 127.8, 127.9, 128.4, 129.3, 129.8, 130.6, 130.88, 130.90, 131.4, 136.5, 145.9, 166.6. − MS (80 eV, 180 °C): *m/z* (%) = 350 (100) $[M]^+$, 322 (16), 305 (4), 276 (28), 202 (7), 138 (8). − IR (KBr): ṽ = 1719 cm^{-1} (CO, vs). − HRMS: *m/z* calcd. for $C_{25}H_{18}O$ 350.13068; found 350.12470.

Ethyl 3-Methyl-4-(pyren-1-yl)benzoate (5g): M.p. 131 °C. − R_f = 0.45 (hexane/ethyl acetate, 6:1). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.48 (t, 3 H), 2.12 (s, 3 H), 4.48 (q, 2 H), 7.46 (d, ^3J = 7.5 Hz, 1 H), 7.66 (d, ^3J = 10.0 Hz, 1 H), 7.84 (d, ^3J = 7.5 Hz, 1 H), 7.96−8.24 (m, 9 H). − ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.4, 20.2, 61.0, 124.5, 124.6, 124.7, 124.8, 125.1, 125.3, 126.7, 126.8, 127.3, 127.5, 127.7, 128.5, 129.7, 130.8, 131.0, 131.3, 136.1, 137.3, 145.5, 166.8. − MS (80 eV, 180 °C): *m/z* (%) = 364 (100) $[M]^+$, 336 (7), 319 (5), 276 (15), 138 (11). − IR (KBr): ṽ = 1706 cm^{-1} (CO, vs). − $C_{26}H_{20}O_2$ (364.44): calcd. C 85.69, H 5.53; found C 85.44, H 5.58.

1-[4-(Pyren-1-yl)phenyl]ethanone (5h): M.p. 184−185 °C. − R_f = 0.22 (hexane/ethyl acetate, 6:1). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.69 (s, 3 H), 7.64 (d, ^3J = 8.2 Hz, 2 H), 7.91 (d, ^3J = 7.9 Hz, 1 H), 7.97−8.21 (m, 10 H). − ^{13}C NMR (126 MHz, $CDCl_3$): δ = 26.6, 124.6, 124.8, 125.0, 125.3, 126.1, 127.2, 127.2, 127.7, 127.8, 128.2, 128.3, 130.7, 130.9, 131.3, 135.7, 136.1, 146.1, 197.7. − MS (70 eV, 315 °C): *m/z* (%) = 320 (100) $[M]^+$, 305 (6), 276 (51), 138 (13). − IR (KBr): ṽ = 1681 (CO, vs) cm^{-1}. − HRMS: *m/z* calcd. for $C_{24}H_{16}O$ 320.120115; found 320.12341.

1-(4-Nitrophenyl)pyrene (5i): M.p. 206−207 °C. − R_f = 0.36 (hexane/ethyl acetate, 6:1). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.77 (d, ^3J = 8.8 Hz, 2 H), 7.93 (d, ^3J = 7.9 Hz, 1 H), 8.00−8.25 (m, 8 H), 8.39 (d, ^3J = 8.8 Hz, 2 H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 123.6, 124.1, 124.7, 124.9, 125.3, 125.7, 126.3, 127.1, 127.2, 128.1, 128.2, 128.4, 130.7, 131.3, 134.8, 147.0, 148.0. − MS (80 eV, 250 °C): *m/z* (%) = 323 (100) $[M]^+$, 276 (46), 138 (12). − IR (KBr): ṽ = 1539 (N=O [ν_{as}], vs), 1342 cm^{-1} (N=O [ν_s], vs). − $C_{22}H_{13}NO$ (323.34): calcd. C 81.72, H 4.03, N 4.33; found C 81.66, H 4.14, N 4.19.

1-(4-Trifluoromethylphenyl)pyrene (5j): M.p. 133 °C. − R_f = 0.54 (hexane/ethyl acetate, 6:1). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.72 (d, ^3J = 8.0 Hz, 2 H), 7.83 (d, ^3J = 8.0 Hz, 2 H), 7.93 (d, ^3J = 8.0 Hz, 1 H), 7.97−8.07 (m, 3 H), 8.09 (s, 2 H), 8.13−8.23 (m, 3 H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 122.3, 124.6, 124.7, 124.9, 125.1, 125.4, 125.5, 126.2, 126.7, 127.3, 127.8, 128.0, 128.4, 129.2, 129.7, 130.9, 131.0, 131.4, 135.9, 144.9. − MS (80 eV, 120 °C): *m/z* (%) = 346 (100) [M$^+$], 276 (57), 138 (22). − IR (KBr): ṽ = 1615 (m), 1327 cm^{-1} (vs, br). − $C_{23}H_{13}F_3$ (346.35): calcd. C 79.76, H 3.78; found C 79.55, H 3.88.

1-(4-Methoxyphenyl)pyrene (5k): M.p. 160 °C. − R_f = 0.51 (hexane/ethyl acetate, 3:1). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 3.92 (s, 3 H), 7.09 (d, ^3J = 8.3 Hz, 2 H), 7.56 (d, ^3J = 8.3 Hz, 2 H), 7.94−8.21 (m, 9 H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 55.4, 113.9, 124.6, 124.7, 125.0, 125.4, 126.0, 127.25, 127.32, 127.4, 127.5, 127.7, 128.6, 130.4, 131.02, 131.04, 131.60, 133.6, 137.5, 159.0. − MS (70 eV, 150 °C): *m/z* (%) = 308 (100) $[M]^+$, 293 (19), 263 (24). − HRMS: *m/z* calcd. for $C_{23}H_{16}O$ 308.120115; found 308.12432.

1-(4-Methoxy-2-methylphenyl)pyrene (5l): M.p. 131 °C. − R_f = 0.53 (hexane/ethyl acetate, 3:1). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.03 (s, 3 H), 3.92 (s, 3 H), 6.91 (d, ^3J = 7.5 Hz, 1 H), 6.95 (s, 1 H), 7.27 (d, ^3J = 7.5 Hz, 1 H), 7.74 (d, ^3J = 9.0 Hz, 1 H), 7.86 (d, ^3J = 7.5 Hz, 1 H), 7.98 (m, 2 H), 8.09 (s, 2 H), 8.14 (d, ^3J = 7.5 Hz, 1 H), 8.19 (t, ^3J = 7.5 Hz, 2 H). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.6, 55.3, 110.9, 115.4, 124.5, 124.8, 124.9, 125.0, 125.5, 125.9, 127.2, 127.3, 127.4, 127.8, 129.3, 130.4, 131.0, 131.4, 131.7, 133.1, 137.1, 138.4, 159.1. − MS (80 eV, 150 °C): *m/z* (%) = 317 (100) $[M]^+$. − HRMS: *m/z* calcd. for $C_{24}H_{18}O$ 322.135765; found 322.13369.

1-(4-Methoxy-2,6-dimethylphenyl)pyrene (5m): M.p. 139 °C. − R_f = 0.54 (hexane/ethyl acetate, 3:1). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.46 (s, 6 H), 3.39 (s, 3 H), 7.32 (s, 2 H), 7.95−8.06 (m, 3 H), 8.08 (s, 2 H), 8.14−8.22 (m, 3 H), 8.27 (d, ^3J = 10.0 Hz, 1 H). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.2, 59.8, 124.5, 124.7, 124.9, 124.9, 125.5, 125.9, 127.18, 127.22, 127.4, 127.5, 128.5, 130.3, 130.7, 131.0, 131.5, 136.6, 137.6, 156.4. − MS (70 eV, 180 °C): *m/z* (%) = 336 (100) $[M]^+$, 321 (23), 306 (15), 276 (10), 138 (7). − HRMS: *m/z* calcd. for $C_{25}H_{20}O$ 336.15141; found 336.151140.

4,4-Dimethyl-2-[4-(pyren-1-yl)phenyl]-2-oxazoline (5n): M.p. 139 °C. − R_f = 0.09 (hexane/ethyl acetate, 6:1). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.47 (s, 6 H), 4.18 (s, 2 H), 7.68 (d, ^3J = 7.5 Hz, 2 H), 7.93 (d, ^3J = 8.0 Hz, 1 H), 7.95−8.00 (m, 2 H), 8.03 (s, 2 H), 8.09−8.21 (m, 6 H). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.4, 67.5, 79.0, 124.5, 124.6, 124.69, 124.73, 124.8, 125.1, 125.9, 126.8, 127.2, 127.5, 127.6, 128.2, 130.4, 130.5, 130.66, 130.69, 131.2, 136.5, 144.1, 161.9. − MS (70 eV, 175 °C): *m/z* (%) = 375 (100) $[M]^+$. − IR (KBr): ṽ = 1644 cm^{-1} (Ar−C=N−R, s). − $C_{27}H_{21}NO$ (375.46): calcd. C 86.37, H 5.64, N 3.73; found C 86.15, H 5.90, N 3.64.

5-(Pyren-1-yl)-2,2′-bipyridine (5o): M.p. 172−173 °C. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34 (t, ^3J = 5.0 Hz, 1 H), 7.86 (dt, ^3J = 7.5, ^4J = 1.5 Hz, 1 H), 7.97−8.25 (m, 10 H), 8.52 (d, ^3J = 8.0 Hz, 1 H), 8.61 (d, ^3J = 8.0 Hz, 1 H), 8.75 (d, ^3J = 5.0 Hz, 1 H), 8.97 (d, ^4J = 1.5 Hz, 1 H). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 120.7, 121.1, 123.8, 124.3, 124.6, 124.7, 124.9, 125.1, 125.4, 126.1, 127.2, 127.5, 127.8, 128.1, 128.6, 130.7, 131.1, 131.3, 133.3, 136.8, 137.0, 138.7, 149.2, 150.4, 154.7, 155.8. − MS (80 eV, 130 °C): *m/z* (%) = 356 (100) $[M]^+$. − HRMS: *m/z* calcd. for $C_{26}H_{16}N_2$ 356.13135; found 356.13467.

4-[(Pyren-1-yl)methyl]benzonitrile (12): Pyrene (7.05 g, 34.86 mmol) and 4-cyanobenzoyl chloride (5.86 g, 35.41 mmol, 1.02 equiv.) were dissolved in carbon disulfide (50 mL) and the mixture was cooled to 0 °C. After the portionwise addition of $AlCl_3$ (6.80 g, 51.00 mmol, 1.46 equiv.), the mixture was heated under reflux overnight, then poured into ice-water (50 g) and the resulting mixture was stirred until the color of the organic phase turned from black to yellow. The layers were then separated, the aqueous phase was extracted with toluene (3 ×), the combined organic phases were dried with $MgSO_4$, and the solvent was evaporated. The residue was purified by column chromatography on silica gel (dichloromethane) and precipitated from dichloromethane/methanol. Yield: 8.34 g (71%) of **12** as bright-yellow crystals; m.p. 171 °C. − R_f = 0.21 (hexane/ethyl acetate, 6:1). − ^{1}H NMR (270 MHz, $CDCl_3$):

δ = 7.71 (d, ^3J = 8.0 Hz, 2 H), 7.91 (d, ^3J = 8.0 Hz, 2 H), 7.96−8.25 (m, 8 H), 8.39 (d, ^3J = 9.5 Hz, 1 H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 116.1, 117.9, 123.7, 124.19, 124.25, 124.8, 126.2, 126.5, 126.6, 127.0, 127.3, 129.5, 129.7, 130.0, 130.5, 130.6, 131.0, 131.1, 132.2, 133.7, 142.2, 196.5. − MS (80 eV, 150 °C): *m/z* (%) = 331 (100) $[M]^+$. − IR (KBr): ṽ = 2229 cm^{-1} (CN, m). − $C_{24}H_{13}NO$ (331.37): calcd. C 86.99, H 3.95, N 4.23; found C 86.86, H 4.02, N 4.00.

As the sole product of the reduction of **12** with sodium borohydride/aluminium chloride in tetrahydrofuran, 4-[hydroxy(pyren-1-yl)methyl]benzonitrile was obtained; m.p. 133 °C. − R_f = 0.16 (hexane/ethyl acetate, 3:1). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.39 (s, 1 H, OH), 6.60 (s, 1 H), 7.37 (d, ^3J = 8.3 Hz, 2 H), 7.42 (d, ^3J = 8.3 Hz, 2 H), 7.87 (d, ^3J = 7.8 Hz, 1 H), 7.95−8.03 (m, 4 H), 8.06 (d, ^3J = 7.8 Hz, 1 H), 8.10−8.16 (m, 3 H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 72.6, 110.7, 118.8, 122.5, 124.5, 124.8, 124.9, 125.0, 125.3, 125.6, 126.1, 127.0, 127.2, 127.8, 128.0, 128.1, 130.3, 131.1, 131.2, 132.0, 135.3, 148.7. − MS (80 eV, 60 °C): *m/z* (%) = 333 (100) $[M]^+$. − IR (KBr): ṽ = 2230 cm^{-1} (CN, s). − HRMS: *m/z* calcd. for $C_{24}H_{15}NO$ 333.11536; found 333.11734.

1-(4-Bromobenzoyl)pyrene (13): M.p. 173 °C (dichloromethane) [174−175 °C (acetic acid)[54]]. − R_f = 0.25 (hexane/ethyl acetate, 10:1). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.59 (d, ^3J = 8.5 Hz, 2 H), 7.74 (d, ^3J = 8.5 Hz, 2 H), 8.02 (d, ^3J = 7.8 Hz, 1 H), 8.06−8.25 (m, 7 H), 8.31 (d, ^3J = 9.3 Hz, 1 H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 123.7, 124.3, 124.5, 124.8, 126.0, 126.2, 126.5, 126.9, 127.1, 128.4, 129.0, 129.3, 129.7, 130.6, 131.1, 131.8, 132.0, 132.4, 133.2, 137.5, 197.3. − MS (80 eV, 150 °C): *m/z* (%) = 386 (100) $[C_{23}H_{13}{}^{81}BrO]^+$, 384 (94) $[C_{23}H_{13}{}^{79}BrO]^+$. − IR (KBr): ṽ = 1651 cm^{-1} (CO, vs). − $C_{23}H_{13}BrO$ (385.26): calcd. C 71.71, H 3.40; found C 71.59, H 3.35.

1-(4-Bromobenzyl)pyrene (14): Ketone **12** (10.5 g, 27.25 mmol) and sodium borohydride (5.12 g, 135.3 mmol, 4.97 equiv.) were dissolved in tetrahydrofuran (200 mL) and aluminium chloride was cautiously added at room temperature. The mixture was heated under reflux for 90 min and then poured into ice-water (200 g). The resulting mixture was extracted with dichloromethane (2 ×), the combined organic phases were dried with $MgSO_4$, and the solvent was evaporated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate, 20:1) and the product was recrystallized from dichloromethane/methanol to give 7.60 g (75%) of **13** as colorless crystals; m.p. 140 °C. − R_f = 0.37 (hexane/ethyl acetate, 10:1). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.63 (s, 2 H), 7.05 (d, ^3J = 8.1 Hz, 2 H), 7.37 (d, ^3J = 8.1 Hz, 2 H), 7.81 (d, ^3J = 7.8 Hz, 1 H), 7.97−8.19 (m, 8 H). − ^{13}C NMR (126 MHz, $CDCl_3$): δ = 38.6, 119.2, 123.4, 124.7, 124.8, 124.9, 125.1, 125.1, 125.9, 127.0, 127.4, 128.0, 129.0, 130.3, 130.7, 131.2, 131.5, 133.6, 140.0. − MS (70 eV, 120 °C): *m/z* (%) = 372 (100) $[C_{23}H_{15}{}^{81}Br]^+$, 370 (98) $[C_{23}H_{15}{}^{79}Br]^+$. − $C_{23}H_{15}Br$ (371.27): calcd. C 74.41, H 4.07; found C 74.27, H 4.01.

As a side product, the incompletely reduced 1-(4-bromophenyl)-1-(pyren-1-yl)methanol was obtained; m.p. 156 °C. − R_f = 0.31 (hexane/ethyl acetate, 3:1). − ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 6.45 (d, 1 H, OH), 6.75 (d, ^3J = 4.5 Hz, 1 H), 7.40 (d, ^3J = 8.2 Hz, 2 H), 7.47 (d, ^3J = 8.2 Hz, 1 H), 8.02 (t, ^3J = 7.6 Hz, 1 H), 8.11−8.33 (m, 7 H). − ^{13}C NMR (63 MHz, [D$_6$]DMSO): δ = 71.8, 120.7, 124.1, 124.6, 124.8, 125.6, 125.8, 126.0, 126.3, 127.0, 127.7, 127.8, 128.0, 128.7, 129.7, 129.6, 130.7, 131.4, 131.7, 138.6, 145.04, 145.08. − MS (80 eV, 60 °C): *m/z* (%) = 388 (31) $[C_{23}H_{15}O^{81}Br]^+$, 386 (30) $[C_{23}H_{15}O^{79}Br]^+$, 203 (100) [pyrene + H]$^+$. − IR (KBr): ṽ = 3260 (s, br), 3041, 2922, 1588 (m), 1484 (s) cm^{-1}. − HRMS: *m/z* calcd. for $C_{23}H_{15}BrO$ 386.03063; found 386.03265.

4-(Pyren-1-ylmethyl)benzonitrile (10): Bromoarene **13** (3.77 g, 10.15 mmol) and copper(I) cyanide (4.65 g, 51.92 mmol, 5.12 equiv.) were suspended in DMF (5 mL) and the mixture was heated at 160 °C overnight. The solvent was then distilled off, the residue was chromatographed on silica gel (CH_2Cl_2), and the product was precipitated from the eluate by adding methanol to give 3.22 g (80%) of **10** as a colorless solid; m.p. 141 °C. − R_f = 0.21 (hexane/ethyl acetate, 6:1). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.62 (s, 2 H), 7.13 (d, ^3J = 8.1 Hz, 2 H), 7.39 (d, ^3J = 8.1 Hz, 2 H), 7.72 (d, ^3J = 7.5 Hz, 1 H), 7.88−7.98 (m, 5 H), 8.02 (m, 3 H). − ^{13}C NMR (126 MHz, $CDCl_3$): δ = 39.2, 119.0, 123.1, 124.7, 124.9, 125.1, 126.1, 127.2, 127.3, 127.9, 128.1, 128.2, 129.0, 129.2, 130.5, 131.2, 132.2, 132.4, 132.4, 146.7. − MS (70 eV, 180 °C): *m/z* (%) = 317 (100) $[M]^+$, 215 (20). − IR (KBr): ṽ = 2224 cm^{-1} (CN, vs). − $C_{24}H_{15}N$ (317.38): calcd. C 90.82, H 4.76, N 4.41; found C 90.44, H 4.56, N 4.14.

4-[2-(Pyren-1-yl)vinyl]benzonitrile (18): Potassium *tert*-butoxide (16.5 g, 147.0 mmol, 1.05 equiv.) was added to a stirred slurry of (4-cyanobenzyl)triphenylphosphonium bromide (64.0 g, 140.0 mmol, 1.36 equiv.) in dry tetrahydrofuran (250 mL). After stirring the resultant solution for 30 min at ambient temperature, pyrene carbaldehyde **15** (23.9 g, 103.4 mmol) was added in a single portion. The mixture was stirred for 2 h at room temperature and then refluxed overnight. After the addition of a molar excess of water, the organic solvent was removed under reduced pressure and the resultant aqueous mixture was extracted three times with dichloromethane. The combined organic layers were dried, filtered, and concentrated to dryness. Column chromatography (hexane/ethyl acetate, 20:1 to 5:1) gave (*E*/*Z*)-**18** (31.5 g, 92%). The (*E*)-isomer was separated by recrystallization from dichloromethane/methanol; m.p. 189 °C. − R_f = 0.20 (hexane/ethyl acetate, 6:1). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.23 (d, ^3J = 16.0 Hz, 1 H), 7.62 (s (!), 4 H), 7.99−8.08 (m, 3 H), 8.11−8.15 (m, 2 H), 8.18−8.20 (m, 3 H), 8.25 (d, ^3J = 8.0 Hz, 1 H), 8.40 (d, ^3J = 9.6 Hz, 1 H). − ^{13}C NMR (126 MHz, $CDCl_3$): δ = 110.5, 119.0, 122.5, 123.6, 124.8, 125.0, 125.1, 125.4, 125.7, 126.2, 126.9, 127.4, 127.8, 128.0, 128.7, 129.1, 129.4, 130.5, 130.7, 131.4, 131.5, 132.5, 142.0. − MS (80 eV, 180 °C): *m/z* (%) = 329 (100) $[M]^+$. − IR (KBr): ṽ = 2215 cm^{-1} (CN, s). − HRMS: *m/z* calcd. for $C_{25}H_{15}N$ 329.12045; found 329.12423. − The (*E*/*Z*) mixture of **18** showed additional signals due to the (*Z*)-isomer in the ^{1}H NMR spectrum: δ = 6.88 (d, ^3J = 12.0 Hz, 1 H), 7.09 (d, ^3J = 8.0 Hz, 2 H), 7.28 (d, ^3J = 8.0 Hz, 2 H), 7.47 (d, ^3J = 12.0 Hz, 1 H), 7.74 (d, ^3J = 8.0 Hz, 1 H).

4-[2-(Pyren-1-yl)ethyl]benzonitrile (17): A mixture of 4-[2-(pyren-1-yl)vinyl]benzonitrile **18** (26.01 g, 78.96 mmol), magnesium (19.27 g, 792.68 mmol, 10.04 equiv.), and 10% Pd/C (3.25 g) in *n*-propanol (1500 mL) was heated to reflux for 24 h. The mixture was then filtered through Celite eluting with tetrahydrofuran. The solvent was removed from the eluate and the residue was purified by column chromatography on silica gel (dichloromethane) to give 25.10 g (96%) of **17**; m.p. 126 °C. − R_f = 0.22 (hexane/ethyl acetate, 6:1). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.16 (t, 2 H), 3.59 (t, 2 H), 7.19 (d, ^3J = 8.0 Hz, 2 H), 7.51 (d, ^3J = 8.0 Hz, 2 H), 7.67 (d, ^3J = 8.0 Hz, 1 H), 7.98−8.06 (m, 4 H), 8.10 (d, ^3J = 9.0 Hz, 1 H), 8.17−8.20 (m, 3 H). − ^{13}C NMR (126 MHz, $CDCl_3$): δ = 34.9, 37.9, 109.8, 119.0, 122.8, 124.7, 124.9, 125.0, 125.1, 125.9, 126.8, 127.2, 127.4, 127.5, 128.5, 129.3, 130.0, 130.7, 131.3, 132.1, 134.5, 147.1. − MS (80 eV, 120 °C): *m/z* (%) = 331 (13) $[M]^+$, 215 (100) $[M - CH_2PhCN]^+$. − IR (KBr): ṽ= 2224 cm^{-1} (CN, m). − $C_{25}H_{17}N$ (331.41): calcd. C 90.60, H 5.17, N 4.23; found C 90.49, H 5.20, N 4.09.

***rac*-[Bis(2,2′-bipyridine){5-(pyren-1-yl)-2,2′-bipyridine}ruthenium-(II)](PF$_6$)$_2$ (19):** A suspension of **5o** (60 mg, 0.17 mmol) and *cis*/*trans*-bis(2,2′-bipyridine)dichlororuthenium(II)·xH$_2$O (86 mg) in aqueous ethanol (30 mL, 1:1, *v*/*v*) was refluxed for 19 h. The solvent was then evaporated and the residue was chromatographed on silica gel eluting with methanol/2 M aq. NH$_4$Cl/nitromethane (7:2:1). Water was added to the eluate and the resulting mixture was extracted with chloroform. After evaporation of the chloroform, the remaining red solid was redissolved in methanol (3 mL) and a saturated solution of NH$_4$PF$_6$ in methanol (2 mL) was added. After standing overnight, the mixture was centrifuged, the solvent was decanted off, and the residue was dried in vacuo to give **19** (0.15 g, 0.14 mmol, 83%); m.p. > 210 °C (decomp.). − ^{1}H NMR (500 MHz, [D$_3$]acetonitrile): δ = 7.14 (dt, ^3J = 6.7, ^4J = 1.5 Hz, 1 H), 7.40 (m, 5 H), 7.68 (d, ^3J = 5.7 Hz, 1 H), 7.73 (dt, ^3J = 7.5, ^4J = 1.5 Hz, 1 H), 7.81 (t, ^3J = 6.0 Hz, 2 H), 7.85 (s, ^4J = 2.2 Hz, 1 H), 7.89 (m, 2 H), 8.00 (d, ^3J = 5.7 Hz, 1 H), 8.04−8.14 (m, 7 H), 8.18 (dt, ^3J = 7.7, ^4J = 1.5 Hz, 1 H), 8.22 (d, ^3J = 8.2 Hz, 1 H), 8.24 (d, ^3J = 7.7 Hz, 1 H), 8.29 (d, ^3J = 8.2 Hz, 2 H), 8.45 (d, ^3J = 8.2 Hz, 1 H), 8.51 (d, ^3J = 8.2 Hz, 2 H), 8.61 (d, ^3J = 8.2 Hz, 1 H), 8.64 (d, ^3J = 8.2 Hz, 1 H), 8.67 (d, ^3J = 8.2 Hz, 1 H). − ^{13}C NMR (125 MHz, [D$_3$]acetonitrile): δ = 123.6, 124.8, 125.0, 125.1, 125.1, 125.2, 125.8, 126.5, 126.9, 127.5, 127.7, 128.0, 128.2, 128.4, 128.4, 128.5, 128.7, 128.8, 129.3, 129.4, 131.2, 131.3, 132.0, 132.5, 138.3, 138.7, 138.7, 138.9, 139.9, 140.9, 152.6, 152.6, 152.6, 152.7, 152.8, 156.4, 157.6, 157.7, 157.7, 157.8. − MS (FAB): *m*/*z* (%) = 915 (4) [M − PF$_6$]$^+$, 770 (1) [M − 2PF$_6$]$^+$, 614 (2) [M − 2 PF$_6$ − bipy]$^+$, 455 (1) [M − 2 PF$_6$ − 2 bipy]$^+$, 413 (4) [Ru(bipy)$_2$]$^+$, 357 (2) [pyrene + bipy]$^+$. − C$_{46}$H$_{32}$F$_{12}$N$_6$P$_2$Ru (1059.79): calcd. C 52.13, H 3.04, N 7.93; found C 51.67, H 3.25, N 7.70.

X-ray Structure Analysis:[63] Crystals of **19** suitable for X-ray structure analysis were obtained by slow diffusion of methanol into a solution of the compound in dichloromethane. A crystal of dimensions 0.65 × 0.53 × 0.20 mm was mounted on tip of a glass fiber at −150 °C and placed in the cold nitrogen stream of a Bruker AXS SMART CCD diffractometer [Mo-K_α radiation (λ = 0.71073 Å), graphite monochromator]. To avoid loss of the intercalated solvent, the data collection was performed at −120 °C. The crystals were found to belong to the monoclinic space group (*C*2/*c*), a = 20.926(3), b = 12.369(2), c = 41.031(6) Å, β = 93.113(2)°, V = 10604(3) Å^3, Z = 8, 2θ$_{max}$ = 27.51°; 11920 unique reflections. The asymmetric unit contains three molecules of dichloromethane per formula unit. The structure was solved by direct methods and full-matrix least-squares refinement against F^2; non-H atoms anisotropic.[78] $R1$ (all data) = 0.0674, $wR2$ = 0.1530; $R1$ = 0.0589, $wR2$ = 0.1480 for 11920 reflections with $F \geq 2\sigma_F$.

Acknowledgments

Financial support by the Deutsche Forschungsgemeinschaft (DFG, Sonderforschungsbereich 448, TP A1 and B3) and the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Lars Hoffmann and Alexander Jagst for their skillful help with some of the experiments, Dr. A. Schäfer for recording the 2D NMR spectra, T. Kohlrep for carrying out the HPLC separations, and A. Rothe for recording the UV absorption and fluorescence spectra.

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Received May 31, 2001
[O01261]