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Photophysical properties of 1,3,6,8-tetrakis(arylethynyl)pyrenes with donor or acceptor substituents: their fluorescence solvatochromism and lightfastness

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ABSTRACT

We prepared a series of 1,3,6,8-tetrakis(arylethynyl)pyrenes with donor or acceptor substituents and investigated their photophysical properties. Solvent polarity hardly affected on the UV/vis spectra of all of the tetrakis(arylethynyl)pyrenes used in this study. On the other hand, electron-donating groups, NMe_2 and NPh_2 groups imparted fluorescence solvatochromicity to the skeleton by intramolecular charge transfer in the excited state. Furthermore, a tetrakis(arylethynyl)pyrene showed better lightfastness upon exposure to laboratory weathering using a xenon long arc lamp than coumarin.

1. Introduction

Acetylene has been widely employed for linking π-conjugated units and for effectively extending the π-conjugation. The progress of such π-conjugated materials by means of acetylene chemistry has strongly depended on the development of Sonogashira coupling reaction.[1] Thereby, many attractive acetylene-linked molecules have emerged such as for semiconducting polymers,[2] macrocyclic molecules,[3] helical polymers,[4] and energy transfer cassettes.[5] Previously, we have synthesized a variety of alkynylpyrene derivatives from mono- to tetrabromopyrenes and arylacetylenes by Sonogashira coupling reaction, and comprehensively examined their photophysical properties.[6] The alkynylpyrenes thus prepared showed not only long absorption and emission wavelengths but also high fluorescence quantum yields as compared with pyrene itself. Additionally, the alkynylpyrene skeleton could be applied to practically useful fluorescence probes for proteins and DNAs. Other research groups have reported that mono-substituted (arylethynyl)pyrenes such as [4-(*N*,*N*-dimethylamino)phenylethynyl]pyrene display fluorescence solvatochromism by intramolecular charge transfer (ICT) mechanism.[7] Recently, interesting papers have been published by Kim et al., in which tetrakis [4-(*N*,*N*-dimethylamino)phenylethynyl]pyrene shows two-photon absorption and electroluminescence properties.[8,9] However, systematic studies on the variously substituted (arylethynyl)pyrenes remain elusive especially for their photophysical characteristics. We also have been investigating the photophysical properties of various (arylethynyl)pyrene derivatives.[6,10] Here we report the comprehensive studies on photophysical properties of tetrakis(arylethynyl)pyrenes with donor or acceptor substituents.

2. Results and discussion

2.1. Synthesis of tetrakis(arylethynyl)pyrenes

Figure 1 shows the chemical structures of tetrakis(arylethynyl)pyrenes **1**–**5** used in this study. These compounds consist of pyrene, acetylene, and aryl moieties: the aryl moieties include R substituents at the *para* position against the acetylene one, and the R is electron-donating, H, or electron-withdrawing group.[10] Pyrene itself is electrically neutral, so that its electric characteristic will depend on those of the R substituents through π-conjugation. Therefore, when the R is an electron-donating group, the pyrene moiety is envisaged to behave as an acceptor, and vice versa. The tetrakis(arylethynyl)pyrenes **1**–**5** were prepared by Sonogashira coupling reaction of tetrabromopyrene with the corresponding arylacetylenes (Fig. 1). Although we synthesized two more acceptor-modified tetrakis(arylethynyl)pyrenes (R=NO_2, CN) in addition to **4** and **5**, they were hardly purified because of their poor solubilities in common solvents.

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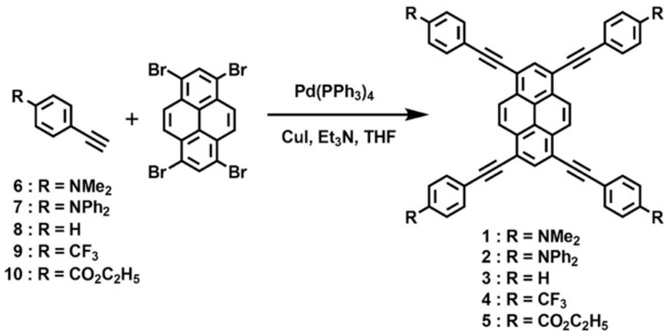

Figure 1. Tetrakis(arylethynyl)pyrenes **1**–**5** and their synthetic scheme.

Furthermore, the poor solubilities hampered us from obtaining clear UV/vis and fluorescence spectra with standard spectrometers.

2.2. Solvatochromism of tetrakis(arylethynyl)pyrenes

To explore the influence of the R substituents upon the absorption and emission of **1**–**5**, their UV/vis and fluorescence spectra were measured at the concentration of 1.0×10^{-6} M in THF. THF was selected because all of **1**–**5** revealed relatively good solubilities in this solvent. The absorption maximum (λ_{abs}) of the neutral **3** was observed at 465 nm (log ε=4.84), which bathochromically shifted by ca. 80 and 60 nm as compared with those of phenylethynylpyrene (382 nm, log ε=4.65) and bis(phenylethynyl)pyrene (407 nm, log ε=4.74) in EtOH, respectively (Fig. 2, Table 1).[6] The bathochromic shift is most likely due to the extension of π-conjugation with increase of the number of phenylethynyl groups on the pyrene core. The molar extinction coefficient also increased with the extension of π-conjugation. The donor-modified **1** (R=NMe_2, 515 nm) and **2** (R=NPh_2, 509 nm) showed much longer absorption maxima than that of the neutral **3**, while the acceptor-modified **4** (R=CF_3) and **5** (R=$CO_2C_2H_5$) were sluggish. The longer absorption maxima for **1** and **2** would be attributed to the electron delocalization between the *para*-substituted donors and the pyrene core through the phenylethynyl moieties.[11] For evaluating the solvatochromism of the tetrakis(arylethynyl)pyrenes, their UV/vis spectra were measured in various solvents, polarities of which increase in the following order: 1,4-dioxane<chloroform<dichloromethane<THF<acetonitrile≃DMF. As shown in Figure S1 in Supplementary data, the donor-modified **1** and **2** showed almost the same UV/vis spectra regardless of solvent polarity, and other tetrakis(arylethynyl)pyrenes also behaved as **1** and **2** did (data not shown).

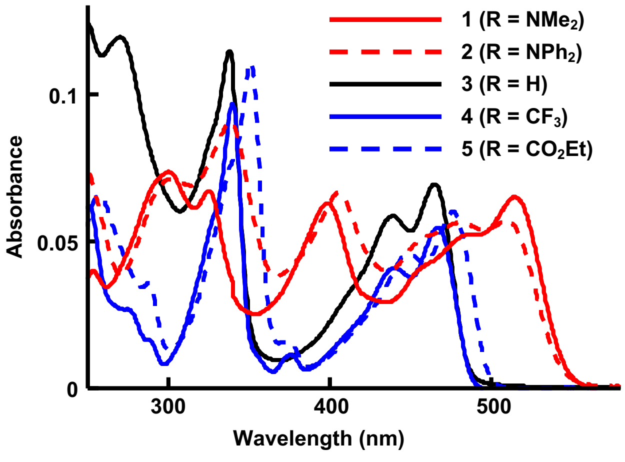

Figure 2. UV/vis spectra of **1**–**5** in THF: [**1**–**5**]=1.0×10^{-6} M.

Table 1
Absorbance and fluorescence data of **1**–**5** in various solvents and a PMMA film

R	Solvents	Absorption[a]		Fluorescence[a]		Stokes' shift (nm)
		λ_{abs}[b] (nm)	log ε (M^{-1} cm^{-1})	λ_{em} (nm)	Φ_f[c]	
1 (NMe2)	1,4-Dioxane	508	4.89	535	0.63	27
	$CHCl_3$	510	4.84	543	0.75	33
	THF	515	4.81	548	0.46	33
	CH_2Cl_2	515	4.86	556	0.59	41
	CH_3CN	513	4.85	619	0.055	106
	DMF	525	4.86	633	0.031	108
	Film[d]	514		54	0.66[e]	30
2 (NPh_2)	THF	509	4.76	546	0.64	37
	Film[d]	512		535	0.32[e]	23
3 (H)	THF	465	4.84	4.81	0.99	16
	Film[d]	464		4.81	0.53[e]	17
4 (CF3)	THF	467	4.74	482	0.98	15
5 (CO_2Et)	THF	476	4.78	494	0.90	18

[a] [**1**–**5**]=1.0×10^{-6} M.

[b] λ_{abs} is the absorption band appearing at the longest wavelength.

[c] Fluorescence quantum yields, determined by fluorescein (Φ_f=0.85 in 0.1 M NaOH) as a reference compound.

[d] The film was prepared from PMMA in THF (19 wt %), and **1**–**3** were dispersed in the film.

[e] Absolute fluorescence quantum yields.

Generally, solvatochromism depends on the extent of charge separation in the ground state of a chromophore. Therefore, density functional theoretical (DFT) calculation was performed for assessing the charge separation in the ground states of **1** and **4**. Figure S2 in Supplementary data displays optimized structures and HOMO and LUMO states for **1** and **4** in a dielectric constant corresponding to $CHCl_3$. The benzene moieties in them adopted coplanar structures against the pyrene core, and all of HOMO and LUMO delocalized. In other solvents, similar results were obtained. Therefore, solvent polarity hardly affects on the ground states of **1** and **4**, supporting no solvatochromicity of the tetrakis(arylethynyl)pyrenes.

2.3. Fluorescence solvatochromism of tetrakis(arylethynyl)pyrenes

Figure 3 shows the normalized-fluorescence spectra of **1**–**5** at the concentration of 1.0×10^{-6} M in THF. The electron-donating **1** and **2** revealed bathochromically shifted emissions than **3**–**5**. The magnitude of the Stokes' shifts for **1** and **2** approximately doubled relative to those for **3**–**5** (Table 1), and the vibronic bands for **1** and **2** tend to deform and broaden. Since THF possesses a moderate

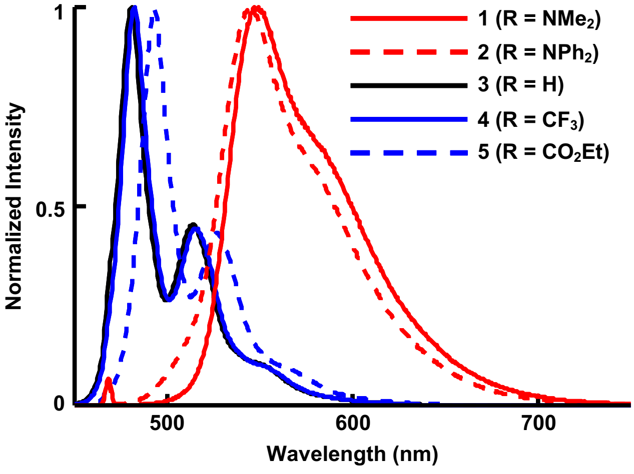

Figure 3. Normalized-fluorescence spectra of **1**–**5** in THF: [**1**–**5**]=1.0×10^{-6} M. All of **1**–**5** were excited at the each λ_{abs} wavelength.

solvent polarity, it might interact with the excited states of the donor-modified alkynylpyrenes. Next, fluorescence spectra for **1**–**5** were measured in various solvents for certifying the influence of solvent polarity on their emission.

Figure 4a and Figure S3 in Supplementary data demonstrate the normalized-fluorescence spectra of **1** and **2**, respectively, in the same series of solvents used for the UV/vis analysis. The emission color for **1** changed from light green in 1,4-dioxane via yellow to red in DMF (Fig. 4b). The Stokes' shifts for **1** and **2** consecutively increased, accompanying the disappearance of their vibronic bands, with increase of the solvent polarity (Table 1 and Table S1 in Supplementary data). In the case of **1**, the difference in the shift spans ca. 80 nm from 1,4-dioxane to DMF. The donor-modified **1** and **2** retained relatively high quantum yields in these solvents except for CH_3CN and DMF. In general, fluorophores, of which emission wavelengths are beyond 600 nm, tend to show low quantum yields caused by the vibrational energy of polar solvents.[12] On the other hand, **3**–**5** did not show such fluorescence solvatochromism (Fig. S4 in Supplementary data). Thus, only donor groups, NMe_2 and NPh_2 were found to afford fluorescence solvatochromicity to the tetrakis(phenylethynyl)pyrene skeleton. The emission wavelength of **1** in DMF is 631 nm, which is ca. 90 nm longer than that of monosubstituted [4-(*N*,*N*-dimethylamino)phenylethynyl]pyrene previously reported by Ho et al.[7b] This longer emission wavelength must be attributed to the tetra-substitution in **1**.

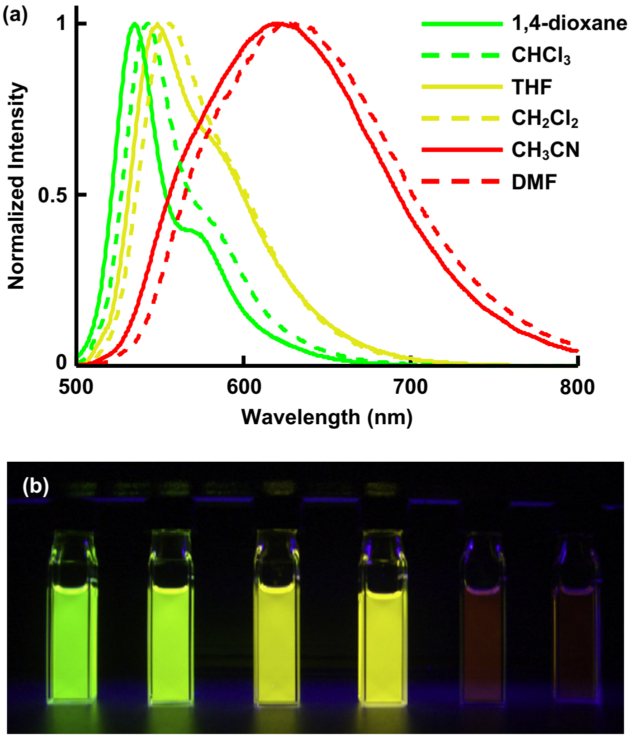

Figure 4. (a) Normalized-fluorescence spectra of **1** at the concentration of 1.0×10^{-6} M in 1,4-dioxane, chloroform, dichloromethane, THF, acetonitrile, and DMF. The excitation wavelength in each solvent was the corresponding λ_{abs} in the solvent. (b) Fluorescence photograph of **1**; solvent polarity increases in the following order from left to right: 1,4-dioxane, chloroform, dichloromethane, THF, acetonitrile, and DMF.

2.4. Origin of fluorescence solvatochromism

Such large Stokes' shift observed for **1** and **2** in polar solvents may result from the difference in the dipole moments between the delocalized ground state and the highly localized excited one. The highly localized excited state must come from the intramolecular charge transfer (ICT) between the NMe_2 (NPh_2) groups and the pyrene core.[7b,13] Relationship between Stokes' shift and the difference in the dipole moments can be related by the Lippert–Mataga equation:

$$\Delta\nu = 2\Delta\mu_{eg}^2\Delta f/hca^3 + const,$$

$$\Delta f = [(\varepsilon-1)/(2\varepsilon+1)] - \left[\left(n^2-1\right)/\left(2n^2+1\right)\right]$$

where $\Delta\nu$ and $\Delta\mu_{eg}$ are Stokes' shift and the difference in the dipole moment between the excited and ground states, respectively; Δf is the orientation polarizability; h is Planck's constant; c is the velocity of light; a is the Onsager radius around a fluorophore; ε is the dielectric constant; n is refractive index.[14–16] To calculate $\Delta\mu_{eg}$, the Stokes' shifts for **1** were plotted against the Δf values in the mixed solvents of 1,4-dioxane and acetonitrile varying their proportion (Fig. 5).[13g] From the slope according to the Lippert–Mataga equation, the $\Delta\mu_{eg}$ value for **1** was estimated to be ca. 30 D, meaning that the dipole moment of **1** drastically changed from the ground to the excited states.[17] On the basis of the large $\Delta\mu_{eg}$ value and the DFT analysis for the ground states, one might suppose that charge separation can exist only in the excited states of the donor-modified tetrakis(phenylethynyl)pyrenes. The Lippert–Mataga plot for the various solvents used in this study also gave a relatively good proportion between the Stokes' shifts of **1** and their Δf values (Fig. S5 in Supplementary data).[13g] The pyrene core in **1** can behave as an acceptor moiety against the dimethylamino groups to give rise to fluorescence solvatochromicity probably based on ICT mechanism. To reinforce the ICT mechanism, time-dependent DFT calculations for **1** and **4** were tried to shed light on their HOMO and LUMO in the excited states.[13b,f] Unfortunately, the calculation hardly converged owing to the molecular size of **1** and **4**. Nevertheless, the findings obtained from UV/vis and fluorescence spectra and Lippert–Mataga analysis imply that the charge separation arises in the excited states of the donor-modified **1** and **2**.

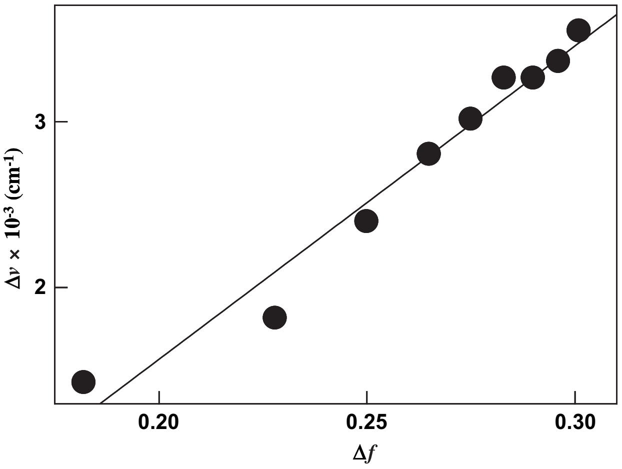

Figure 5. Plots of the Stokes' shift $\Delta\nu$ versus the solvent polarity Δf, derived from fluorescence spectra of **1** in a series of 1,4-dioxane/acetonitrile mixtures; Δf is obtained for each mixture using ε and n values calculated using the molar fractions as follows: $\varepsilon=\chi_{acetonitrile}\times38.8+\chi_{dioxane}\times2.218$; $n=\chi_{acetonitrile}\times1.3442+\chi_{dioxane}\times1.4224$; $\chi_{acetonitrile}+\chi_{dioxane}=1$.

2.5. Photophysical properties of tetrakis(arylethynyl)pyrenes in PMMA films

To assess the possibilities of tetrakis(arylethynyl)pyrenes as a photomaterial, polymethylmethacrylate (PMMA) films of **1**–**3** and coumarin were prepared. Photophysical data (λ_{abs}, λ_{em}, and Φ_f) for **1**–**3** in the film were shown in Table 1. The absorption and emission wavelengths for **1**–**3** in the film almost correspond to those in THF.

The films including **1**–**3** and coumarin were exposed to laboratory weathering using a xenon long arc lamp in order to explore their lightfastness (Fig. 6). After the exposure for 80 h, ca. 30% of **2** survived, whereas most of coumarin underwent degradation. Diarylamino groups were reported to be a good auxofluorophore for imparting photostability to 1,4-distyrylbenzene cores as compared with dialkylamino ones by Kauffman and Monya.[18] The similar substituent effect is considered to work on the 1,3,6,8-tetrakis(phenylethynyl)pyrene core.

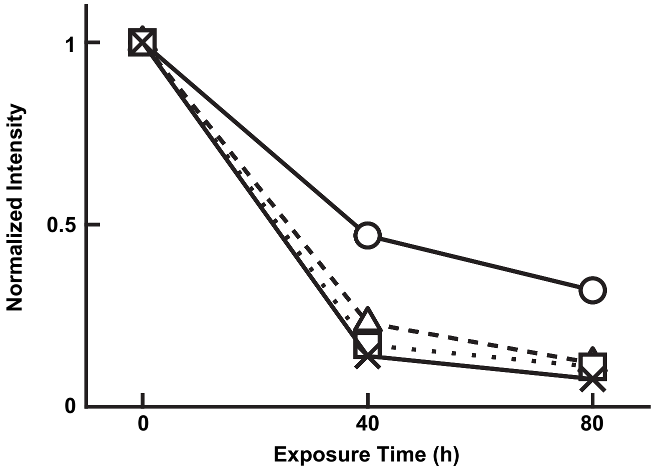

Figure 6. Normalized intensities derived from the excitation spectra of **1**–**3** and coumarin in the PMMA film after exposure to artificial sunlight through a UV-cut filter at 40 °C, plotted against the exposure time: △ for **1**, ○ for **2**, □ for **3**, and × for coumarin. A 6.5 kW xenon long arc lamp was used as a light source. The relative humidity was controlled to be ca. 50%. The samples were fixed away from ca. 310 mm of the light source.

3. Conclusion

In summary, we have developed a variety of 1,3,6,8-tetrakis(arylethynyl)pyrenes bearing electron-donating or electron-withdrawing groups and examined their photophysical properties. The donor-modified tetrakis(arylethynyl)pyrenes showed fluorescence solvatochromism on the basis of ICT mechanism, while the acceptor-modified ones never did. Additionally, a donor-modified tetrakis(arylethynyl)pyrene was found to be stable under laboratory weathering as compared with coumarin. The tetrakis(arylethynyl)pyrenes are expected to be applicable to bioprobes for hydrophobic pockets in various biomolecules and photomaterials.

4. Experimental

4.1. General methods

^{1}H NMR spectra were recorded at 300 MHz. The ^{13}C NMR spectra for 1,3,6,8-tetrakis(arylethynyl)pyrenes could not be measured because their highly concentrated solutions in various common organic solvents were not available due to their poor solubility. Absolute fluorescence quantum yields were measured with a commercial spectrometer equipped with an integrating sphere, radius of which is 3.3 inch. FABMS and MALDI-MS experiments were performed with 3-nitrobenzyl alcohol and retinoic acid as a matrix, respectively. Melting points are uncorrected.

4.2. Materials

Reagents were purchased from commercial sources and used without further purification. The following compounds 1,3,6,8-tetrabromopyrene[19], 4-(dimethylamino)phenylacetylene[20] (**6**), (4-ethynylphenyl)diphenylamine[21] (**7**), [4-(ethoxycarbonyl)phenyl]-acetylene[22] (**10**) were prepared according to published procedures. The 1,3,6,8-tetrakis(arylethynyl)pyrenes **1**,[8] **3**,[19] and **4**[19] published previously were synthesized in the same synthetic procedure as that for **2** and **5** vide infra.

4.3. Spectroscopic measurements in solution

Steady state absorption and emission spectra were recorded at 298 K using a 1 cm pass length cell. Fluorescence quantum yields were determined by using fluorescein (Φ_f=0.85 in 0.1 M NaOH)[23] as a reference compound. The fluorescence quantum yields were calculated according to the following equation.

$$\Phi_{\mathrm{f(sample)}} = \Phi_{\mathrm{f(standard)}} \times \left[A_{\mathrm{standard}}/A_{\mathrm{sample}}\right] \times \left[I_{\mathrm{sample}}/I_{\mathrm{standard}}\right] \times \left[n_{\mathrm{sample}}/n_{\mathrm{standard}}\right]^2$$

In this equation, $\Phi_{\mathrm{f(sample)}}$ and $\Phi_{\mathrm{f(standard)}}$ are the quantum yields of a sample and a standard, respectively. A_{sample}, I_{sample}, and n_{sample} are the optical density, the integrated emission intensity at the excitation wavelength, and the value of refractive index for the sample, respectively. A_{standard}, I_{standard}, and n_{standard} are those for the standard.

4.4. Preparation of PMMA films

Each chromophore was dissolved in a PMMA/THF solution (19 wt %). A PET film (A6 size) was coated with the solution (1.5 mL) including a chromophore by spin coating. After dried up at room temperature for 1 h, the coated film was subjected to various spectroscopic measurements. When a chromophore is hard to be fully dissolved in the medium, its PMMA film was prepared in the dispersed state.

4.5. Computational work

Geometry optimize calculation was carried out for **1** and **4** by using Gaussian 03W program. Hybrid density functional (B3LYP) level of theory in conjunction with 6-31G(d) basis sets has been used.[24]

4.6. Preparation of tetrakis(arylethynyl)pyrenes 2 and 5

*4.6.1. 1,3,6,8-Tetrakis{[4-(N,N′-diphenylamino)phenyl]ethynyl}pyrene (**2**).* A degassed THF/Et$_3$N (150+40 mL) mixed solution of 1,3,6,8-tetrabromopyrene[19] (0.12 g, 0.232 mmol), Pd(t-Bu$_3$P)$_2$ (24 mg, 0.0470 mmol), CuI (4.4 mg, 0.0231 mmol), and (4-ethynylphenyl)diphenylamine[20] (**7**) (0.281 g, 1.04 mmol) was refluxed for 48 h. The reaction mixture was then cooled to room temperature and filtered. The filtrate was evaporated, and the residue was purified by chromatography (silica gel; eluent, CHCl$_3$) to give **2** (red powder): yield 42% (0.124 g); mp >320 °C (dec); IR (KBr): $\tilde{\nu}$ = 2196 cm^{-1}; ^{1}H NMR (THF-d_8) δ=7.06–7.16 (m, 16H), 7.28–7.33 (m, 16H), 7.60 (d, J=8.7 Hz, 8H), 8.39 (s, 2H), 8.78 (s, 4H); MS (MALDI) m/z calcd for $C_{96}H_{62}N_4$: 1270.5; found: 1270.7 [M]$^+$; HRMS (FAB) m/z calcd for $C_{96}H_{63}N_4$: 1271.5053; found: 1271.5026 [M+H]$^+$.

*4.6.2. 1,3,6,8-Tetrakis[(4-ethoxycarbonylphenyl)ethynyl]pyrene (**5**).* A degassed THF/Et$_3$N (30+30 mL) mixed solution of 1,3,6,8-tetrabromopyrene[19] (0.46 g, 0.888 mmol), PdCl$_2$(PPh$_3$)$_2$ (31 mg, 0.0442 mmol), CuI (8.5 mg, 0.0446 mmol), and [4-(ethoxycarbonyl)phenyl]acetylene[21] (**10**) (0.697 g, 4.0 mmol) was refluxed for 24 h. The reaction mixture was then cooled to room temperature and poured into water. The resulting precipitate was filtered and washed with MeOH (100 mL), $CHCl_3$ (100 mL), and benzene (100 mL) successively and dried to give **5** (orange powder): yield 70% (0.554 g); mp >300 °C (dec); IR (KBr): $\tilde{\nu}=1272, 1717, 2201, 2226\ cm^{-1}$; ^1H NMR (THF-d_8) δ=1.41 (t, J=7.2 Hz, 12H), 4.39 (m, 8H), 7.85 (d, J=8.7 Hz, 8H), 8.11 (d, J=8.7 Hz, 8H), 8.53 (s, 2H), 8.83 (s, 4H); HRMS (FAB) m/z calcd for $C_{60}H_{43}O_8$: 891.2958; found: 891.2933 $[M+H]^+$.

Supplementary data

UV/vis spectra of **1** and **2** in various solvents, absorbance and fluorescence data of **2**, graphical presentation for HOMO and LUMO in **1** and **4**, normalized-fluorescence spectra of **2**–**5**, Lippert–Mataga plot of **1**, and ^1H NMR spectra of **2** and **5**. Supplementary data associated with this article can be found in online version, at doi:10.1016/j.tet.2009.08.079.

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