Synthesis, Absorption, and Fluorescence-Emission Properties of 1,3,6,8-Tetraethynylpyrene and Its Derivatives

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Keywords: Alkynes / Conjugation / Fluorescence / Quantum yield / Pyrene

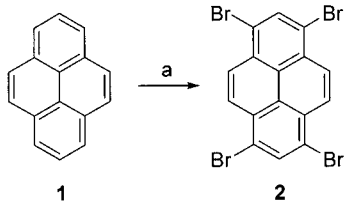
The synthesis of several 1,3,6,8-tetraethynylpyrene derivatives is reported. The effect of extended acetylenic conjugation on their absorption and fluorescence-emission properties is studied. Significant bathochromic shifts of both the absorption and fluorescence emission bands are observed. These derivatives emit fluorescence in the visible (400–550 nm) region.

Introduction

Pyrene (**1**) is a prototypical fluorescent molecule with desirable photophysical properties that make it useful as a fluorescence probe. Pyrene and its derivatives have been widely used as fluorescence probes in many applications. For example, pyrene-labeled oligonucleotides have been used as probes to study DNA hybridization,[1] and pyrene-labeled lipids have been used to study the depth-dependent quenching of fluorescence in lipid bilayers.[2] Recently, the synthesis of a pyrene-based fluorescent dendrimer has been reported wherein the core unit is a 1,3,6,8-tetrasubstituted pyrene and the peripheral units contain monosubstituted pyrene units.[3] In spite of its wide use there are two major drawbacks in using pyrene as a fluorescence probe. The absorption and emission wavelengths of the pyrene monomer are confined to the UV region and pyrene forms an excimer above concentrations of 0.1 mM. In order to probe biological membranes using fluorescence techniques it is desirable to have a fluorophore probe that absorbs and emits in the longer wavelength region, preferably in the visible region of the electromagnetic spectrum in order to minimize the spectral overlap of the intrinsic fluorescence of the biomolecules such as tryptophan, tyrosine, and NADH that occur in the UV region. Furthermore, molecular systems that are light emitters in the visible region are potentially useful in the fabrication of organic light emitting devices (OLED).[4] Therefore it is desirable to design molecules that have emission in the visible region. The most common method to bathochromically shift the absorption and emission characteristics of a fluorophore is to extend the π-conjugation by introducing unsaturated functional groups to the core of the fluorophore. One such group is the acetylenic group. In a recent paper the absorption and fluorescence emission properties of the dimer of 1-ethynylpyrene, namely 1,4-bis(1-pyrenyl)butadiyne, have been reported,[5] and polymers of 1-ethynylpyrene and 1-trimethylsilylethynylpyrene have also been reported.[6] These polymers exhibit high thermal stability and absorb and emit in the visible region. Crystalline oligopyrene nanowires exhibiting multicolored emission have also been reported.[7] In the present study we have used acetylenic groups to extend the conjugation of the pyrene chromophore. We describe the synthesis of 1,3,6,8-tetraethynylpyrene and several of its derivatives bearing both hydrophilic and hydrophobic substituents and studies on the electronic absorption and fluorescence emission properties of these molecules.

Results and Discussion

1,3,6,8-Tetrabromopyrene (**2**)[8] is readily obtained by the exhaustive bromination of pyrene (Scheme 1), and it served as the starting material for the synthesis of 1,3,6,8-tetraethynylpyrene derivatives.



Scheme 1. Synthesis of 1,3,6,8-tetrabromopyrene. Reagents and conditions: (a) Br_2, nitrobenzene, 120 °C, 94% (**2**).

The Sonogashira coupling of tetrabromide **2** with various terminal acetylenes yielded the corresponding tetraethynyl derivatives **3a**–**f** in moderate to good yields (Scheme 2).

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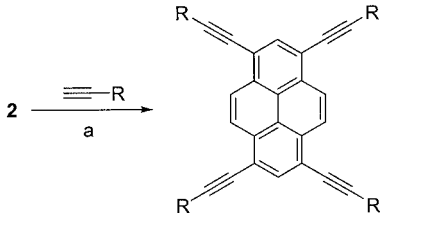
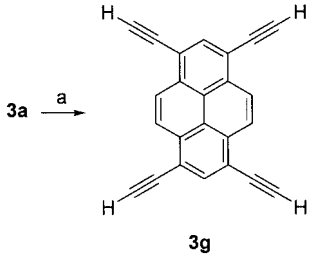


R		Yield (%)
$SiMe_3$	**3a**	33
$C(Me)_2OH$	**3b**	89
CH_2OH	**3c**	65
$CH(OEt)_2$	**3d**	45
C_6H_5	**3e**	93
$4\text{-}CF_3C_6H_4$	**3f**	92

Scheme 2. Synthesis of 1,3,6,8-tetraethynylpyrene derivatives (**3a**–**f**). Reagents and conditions: (a) $[PdCl_2(PPh_3)_2]$, diisopropylamine, PPh_3, CuI, 60–70 °C.

The tetraethynyl derivatives **3a**–**f** possess D_{2h} point-group symmetry; therefore their ^1H NMR spectra are simple and display a pair of singlets in a 2:1 ratio for the pyrene ring protons. The four protons on carbon atoms 4, 5, 9, and 10 appear as a singlet in the region of δ = 8.4–8.6 ppm and the two protons on carbon atoms 2 and 7 appear as a singlet in the region of δ = 8.2–8.3 ppm. The products arising from partial substitution, namely di- and trisubstituted derivatives, give a complex multiplet pattern for the pyrene ring protons in the ^1H NMR spectrum and are readily discernible from the tetrasubstituted derivatives.[9] The tetrakis(trimethylsilylethynyl) derivative **3a** was obtained as an orange solid in 33% yield. Removal of the TMS groups by treatment with tetra-*n*-butylammonium fluoride in THF yielded tetraethynylpyrene **3g** as a pale-yellow solid in 93% yield (Scheme 3).



Scheme 3. Synthesis of 1,3,6,8-tetraethynylpyrene (**3g**). Reagents and conditions: (a) nBu_4NF, THF, room temp., 1 h, 93% (**3g**).

Tetraethynylpyrene (**3g**) is a stable solid that can be stored at room temperature in air for a prolonged period of time. While **3a** is soluble in all the common organic solvents, including hexane, compound **3g** is rather insoluble. The NMR spectra of **3g** were recorded in $[D_8]$THF. Derivatives **3b**–**f** are also highly insoluble in common organic solvents. Nevertheless, the compounds were thoroughly characterized by various spectroscopic techniques. In particular, the MALDI-TOF mass spectra of these derivatives display the molecular ion peak along with the isotope peaks in expected intensity ratios (Figure 1).

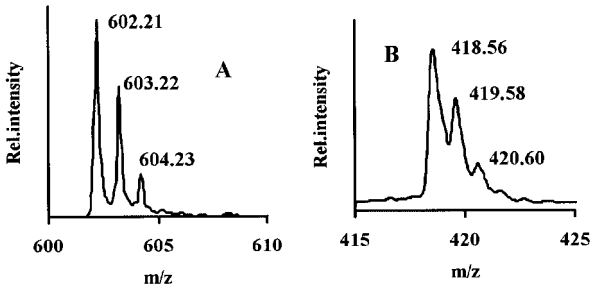
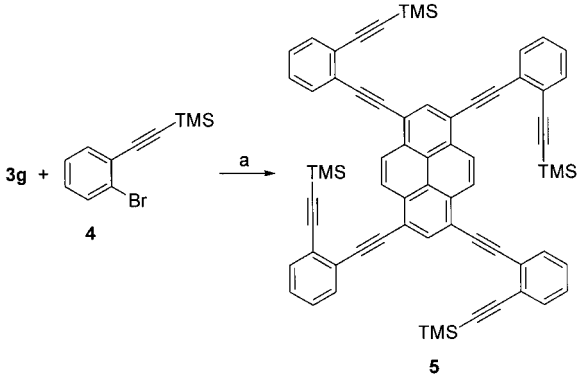


Figure 1. MALDI-TOF mass spectra showing the molecular ion region of **3e** (**A**) and **3c** (**B**) and the isotope peaks.

In order to utilize tetraethynylpyrene (**3g**) as an acetylenic building block to extend the conjugation of the pyrene chromophore we investigated the Sonogashira coupling of **3g**. The coupling of **3g** and 1-bromo-2-(trimethylsilylethynyl)benzene (**4**) gave the expected tetrasubstituted derivative **5**, albeit in poor yield (10%), along with an insoluble red brown solid. Iodoarenes are generally more reactive in the Sonogashira coupling reaction.[10] However, in the present case when 1-iodo-2-(trimethylsilylethynyl)benzene was used instead of **4** no significant improvement in the yield of **5** was observed (Scheme 4).



Scheme 4. Extention of conjugation of pyrene using **3g** as the building block. Reagents and conditions: (a) $[PdCl_2(PPh_3)_2]$, diisopropylamine, PPh_3, CuI, 60–70 °C.

The electronic absorption and fluorescence-emission data along with the quantum yield of fluorescence for compounds **3a**–**g** and **5** are listed in Table 1 and are compared with that of pyrene (**1**).[11] The spectra were recorded in THF, typically in the concentration range of 10^{-5}–10^{-6} M. Therefore, the reported fluorescence data correspond to only the monomer emission. The solutions were degassed by purging with dry N_2 prior to quantum yield measurements. The fluorescence intensity of compounds **3a**–**g** was unaffected by the presence of atmospheric oxygen as the fluorescence intensities of **3a**–**g** are the same before and after degassing.

Typically, three absorption bands were observed in the region 350–450 nm for derivatives **3a**–**d**. The corresponding bands for **3e** and **3f** are bathochromically shifted to the region 375–475 nm (Figure 2). While derivatives **3a**–**d** show well-resolved sharp absorption bands, those of **3e** and **3f** are broad and less resolved. The longest wavelength π–π*

Table 1. Electronic absorption, fluorescence emission, and quantum yield of fluorescence of **3a**–**g** and **5**.[a]

Compound	Absorption λ_{max} [nm] (log ε [$M^{-1}cm^{-1}$])	Fluorescence emission λ_{max} [nm] (λ_{ex})[b]	Φ_f[c]
1	335 (5.10), 319 (5.05), 306 (4.98), 288 (5.05), 272 (5.13), 261 (5.08), 239 (5.34)	393, 389 (sh), 384, 379, 373, (336)	0.60
3a	435 (5.19), 409 (5.05), 387 (4.85), 314 (5.20), 302 (5.01), 289 (4.94), 256 (5.02), 237 (5.08)	498, 465, 439, (389)	0.42
3b	420 (3.71), 358 (4.17), 341 (4.22), 303 (4.34), 290 (4.37), 243 (4.70)	438 (sh), 416, (358)	0.49
3c[d]	420 (4.72), 395 (4.62), 374 (4.45), 307 (4.70), 296 (4.57), 257 (4.59)	481 (sh), 450, 425, (375)	0.68[d]
3d	424 (5.13), 398 (5.02), 377 (4.85), 308 (5.17), 295 (5.01), 254 (5.07)	485, 455, 427, (410)	0.36
3e	462 (4.77), 437 (4.70), 338 (4.97), 240 (4.96)	552 (sh), 512, 480, (485)	0.18
3f	465 (4.42), 438 (4.36), 339 (4.71), 249 (4.65)	552 (sh), 514, 482, (375)	0.16
3g	414 (4.60), 390 (4.47), 370 (4.21), 305 (4.55), 289 (4.53), 252 (4.33), 238 (4.53)	472 (sh), 442, 418, (374)	0.59
5	476 (4.74), 446 (4.59), 420 (sh), 351 (4.87)	558 (sh), 521, 492, (349)	nd

[a] Spectra were measured for 10^{-5}–10^{-6} M solutions in THF. [b] wavelength of excitation. [c] Using anthracene (Φ_f = 0.31) as the fluorescence standard. [d] In DMSO. sh = shoulder, nd = not determined.

bands of pyrene derivatives **3a**–**g** are bathochromically shifted by 85–130 nm in comparison to pyrene[11] due to the extended conjugation of the pyrene chromophore with the acetylenic units. The phenylethynyl derivatives **3e** and **3f** show the largest bathochromic shift of the absorption bands due to the extension of conjugation with the pendent phenyl groups. Similarly, the fluorescence emission bands of **3a**–**g** are also bathochromically shifted in comparison to that of pyrene.[11] For example, compared to the $S_{0,0}$ emission band of pyrene at 373 nm, the $S_{0,0}$ emission band of **3e** and **3f** occur at 480 and 482 nm, respectively, a shift of nearly 90 nm. The lowest energy emission bands of these derivatives occur at 552 nm, well into the visible region, and are about 150 nm bathochromically shifted compared to that of pyrene. The fluorescence spectra are independent of the excitation wavelength. The quantum efficiency of fluorescence was determined using anthracene as the standard fluorophore in THF. The quantum efficiency of fluorescence emission for **3a**–**d** and **3g** was in the range of 0.4–0.7; these values are comparable to that of pyrene. However, the quantum efficiencies of fluorescence for **3e** and **3f** are 0.18 and 0.16, respectively, much lower than that of the other derivatives. In the case of **3a**–**d** the chromophore, namely tetraethynylpyrene, is highly rigid and hence the competing nonradiative pathways do not occur efficiently. In the case of **3e** and **3f** the free rotation of the phenyl substituents that are in conjugation with the pyrene chromophore is possible, allowing competing nonradiative pathways for the decay of the excited singlet state. Furthermore, both the absorption and emission bands of the phenyl-substituted derivatives **3e** and **3f** are much broader than those of **3a**–**d** (Figure 2 and Figure 3).

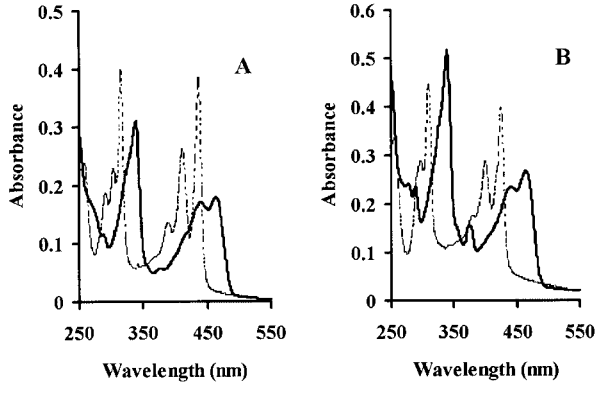


Figure 2. Electronic absorption spectra: (A) **3a** (-----) and **3e** (—); (B) **3d** (----) and **3f** (—) in THF.

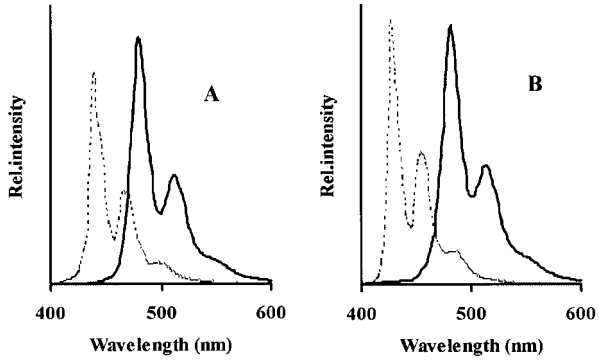


Figure 3. Fluorescence emission spectra: (A) **3a** (----) and **3e** (—); (B) **3d** (----) and **3f** (—) in THF.

Conclusions

The extension of conjugation of the pyrene chromophore by acetylenic substituents has effectively served to shift the wavelength of absorption and fluorescence emission into the visible region of the electromagnetic spectrum. The quantum efficiencies of fluorescence of the tetraethynyl derivatives are comparable to that of pyrene, except in the case of the phenyl-substituted derivatives **3e** and **3f**, whose fluorescence quantum efficiencies are low due to the deactivation of the excited state resulting from the free rotation of the phenyl groups. These derivatives emit fluorescence in the visible region and hence they are potentially useful as organic light emitting materials in the fabrication of light emitting devices.

Experimental Section

General Remarks: ^1H and ^{13}C NMR spectroscopy: Bruker AM-400 or Jeol GSX 400 NB at 400 MHz and 100 MHz, respectively; TMS as internal standard. Mass spectrometry: MALDI-TOF MS with an Applied Biosystems Voyager 6316 spectrometer using either α-cyano-4-hydroxycinnamic acid or tetracyanoethylene as the matrix;

ESI-MS with a Micromass Micro Q-TOF spectrometer; EI-MS with a Finnigan MAT 90X spectrometer. IR spectra were recorded with a Perkin–Elmer Spectrum One spectrometer. UV/Vis spectra were recorded with a Cary 5E Varian UV/Vis/NIR spectrometer. All the fluorescence measurements were made with a Jobin Yvon Horiba Fluorolog-3 spectrometer. The fluorescence quantum yields were measured using anthracene as the standard according to a literature procedure.[12] Although atmospheric oxygen did not affect the fluorescence intensity of compounds **3a**–**g**, the solutions were degassed prior to fluorescence measurements. The quantum yields were corrected for the refractive indices of the solvents used. All reactions were carried out under dry nitrogen in oven-dried Schlenk flasks, unless indicated otherwise. Column chromatography was performed on silica gel (60–120 or 240–400 mesh). TLCs were run on Macherey–Nagel polygram sil G/UV_{254} plates. All the compounds reported herein did not melt up to 200 °C and the temperature for the onset of decomposition, as determined by thermogravimetric analysis, is given in the individual cases. THF was distilled from sodium.

1,3,6,8-Tetrabromopyrene (2):[8] Bromine (35.0 g, 0.22 mol) was added dropwise, with vigorous stirring, to a solution of pyrene (**1**; 10.0 g, 0.049 mol) in nitrobenzene (200 mL) at 120 °C. The mixture was kept at 120 °C for 4 h and then cooled to room temperature to yield a pale-green precipitate. This was filtered, washed with ethanol (150 mL), and dried under vacuum. The solid product (24.1 g, 94%) was insoluble in all the common organic solvents. It was identified as **2** by EI-MS data, which display the isotope peaks in the expected ratio. The product was used as such for the Sonogashira coupling reactions. MS (EI, 70 eV): *m*/*z* (%) = 522 (12), 520 (50), 518 (70), 516 (48), 514 (12) [M^+] (isotope peaks in the ratio 1:4:6:4:1), 441, 439, 438, 437, 435 [M^+ – Br] (isotope peaks), 360 (19), 358 (38), 356 (19) [M^+ – 2 Br], 198 (100) [M^+ – 4 Br].

General Procedure for the Sonogashira Coupling of 2: Compound **2** (1.0 g, 1.93 mmol), [$PdCl_2(PPh_3)_2$] (67 mg, 0.096 mmol), CuI (18 mg, 0.096 mmol), PPh_3 (50 mg, 0.193 mmol), and the terminal alkyne (11.6 mmol) were added to a degassed solution of diisopropylamine (20 mL) and THF (20 mL) under N_2. The resulting mixture was stirred at 60–70 °C for the time mentioned in the individual cases. The reaction mixture was then cooled to room temperature and solvent was removed to give the crude reaction mixture, which was further worked up as indicated in the individual cases.

1,3,6,8-Tetrakis(trimethylsilylethynyl)pyrene (3a): Trimethylsilylacetylene (1.14 g, 11.57 mmol) was used and the reaction was carried out at 65 °C for 12 h. Column chromatographic purification of the crude product on silica gel with hexane as the eluent yielded **3a** (0.38 g, 33%) as a red orange solid. Temperature for onset of decomposition: 325 °C. IR (KBr): $\tilde{\nu}$ = 2958, 2152 cm^{-1} (C≡C). ^1H NMR ($CDCl_3$): δ = 8.53 (s, 4 H), 8.28 (s, 2 H), 0.39 (s, 36 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 134.5, 131.9, 126.8, 123.4, 118.5, 102.8, 101.3, 0.1 ppm. MS (EI, 70 eV): *m*/*z* (%) = 586 (20) [M^+], 490 (100), 179 (70), 73 (55). HRMS: calcd. for $C_{36}H_{42}Si_4$ 586.23636; found 586.23571.

1,3,6,8-Tetrakis(3-hydroxy-3-methyl-1-butynyl)pyrene (3b): 2-Methyl-3-butyn-2-ol (1.62 g, 19.3 mmol) was used and the reaction was carried out at 60 °C for 16 h. The crude product was purified by column chromatography on silica gel using a mixture of hexane/acetone (4:1, v/v) as the eluent to yield **3b** (0.92 g, 89%) as a yellow solid. Temperature for onset of decomposition: 175 °C. IR (KBr): $\tilde{\nu}$ = 3291 cm^{-1} (OH), 2224 (C≡C). ^1H NMR ([D_6]DMSO): δ = 8.43 (s, 4 H), 8.08 (s, 2 H), 5.76 (s, 4 H, OH) 1.70 (s, 24 H) ppm. ^{13}C NMR ([D_6]DMSO): δ = 132.6, 130.4, 126.1, 122.6, 118.2, 103.0, 78.1, 64.0, 31.6 ppm. MALDI-TOF MS: *m*/*z* = 530 [M^+]. HRMS (ESI-MS, MeOH/H_2O): calcd. for $C_{36}H_{34}NaO_4$ 553.2355; found 553.2393 [M + Na^+]; calcd. for $C_{36}H_{35}O_5$ 513.2430; found 513.2451 [M + OH].

1,3,6,8-Tetrakis(3-hydroxy-1-propynyl)pyrene (3c): Propargyl alcohol (0.65 g, 11.6 mmol) was used and the reaction was carried out at 70 °C for 42 h. The crude product was triturated with $CHCl_3$ (25 mL) and the yellow solid obtained was filtered and washed with water and dried to give **3c** as a pale-yellow solid (0.52 g, 65%). Temperature for onset of decomposition: 200 °C. IR (KBr): $\tilde{\nu}$ = 3272 cm^{-1} (OH), 2218 (C≡C). ^1H NMR ([D_6]DMSO): δ = 8.61 (s, 4 H), 8.19 (s, 2 H), 5.60 (t, *J* = 5.7 Hz, 4 H, OH) 4.56 (d, *J* = 5.7 Hz, 8 H) ppm. ^{13}C NMR ([D_6]DMSO): δ = 130.9, 126.5, 118.4, 115.0, 109.4, 97.3, 81.1, 49.7 ppm. MALDI-TOF MS: *m*/*z* (%) = 418 (100) [M^+], 419 (65) [M^+ + 1], 420 (20) [M^+ + 2].

1,3,6,8-Tetrakis(3,3-diethoxy-1-propynyl)pyrene (3d): Toluene (20 mL) was used instead of THF. Propiolaldehyde diethyl acetal (1.23 g, 9.65 mmol) was used and the reaction was stirred at 70 °C for 24 h. The crude product was dissolved in $CHCl_3$ and washed with water (75 mL) followed by saturated brine solution (75 mL). After removal of the solvent, the product was further purified by column chromatography on silica gel using hexane/ethyl acetate (9:1, v/v) to give **3d** as a yellow solid (0.62 g, 45%). Further purification was done by recrystallization from $CHCl_3$. Temperature for onset of decomposition: 238 °C. IR (KBr): $\tilde{\nu}$ = 2222 cm^{-1} (C≡C). ^1H NMR ($CDCl_3$): δ = 8.53 (s, 4 H), 8.26 (s, 2 H), 5.63 (s, 4 H) 3.88 (m, 4 H), 3.74 (m, 4 H), 1.28 (t, *J* = 7.0 Hz, 24 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 134.5, 132.2, 127.1, 123.5, 117.6, 92.0, 91.2, 82.9, 61.2, 15.1 ppm. MALDI-TOF MS: *m*/*z* (%) = 706 (100) [M^+], 707 (65) [M^+ + 1], 708 (25) [M^+ + 2]. ESI-MS: *m*/*z* (%) = 729.5 (82) [M + Na^+], 661.4 (58) [M^+ – OC_2H_5].

1,3,6,8-Tetrakis(phenylethynyl)pyrene (3e): Phenylacetylene (0.89 g, 8.68 mmol) was used and the reaction mixture was heated at 70 °C for 16 h. The yellow precipitate was filtered and washed with $CHCl_3$ (75 mL) and benzene (100 mL) and dried to yield **3e** as a yellow powder (1.08 g, 93%). Temperature for onset of decomposition: 375 °C. IR (KBr): $\tilde{\nu}$ = 2200 cm^{-1} (C≡C). MALDI-TOF MS: *m*/*z* (%) = 602 (100) [M^+], 603 (70) [M^+ + 1], 604 (20) [M^+ + 2]. HRMS (EI, 70 eV): calcd. for $C_{48}H_{26}$ 602.20345; found 602.20505.

1,3,6,8-Tetrakis{[4-(trifluoromethyl)phenyl]ethynyl}pyrene (3f): Triethylamine (10 mL) was used instead of diisopropylamine. 4-(Trifluoromethylethynyl)benzene (0.33 g, 1.93 mmol) was used and the reaction was carried out at 70 °C for 10 h. The orange precipitate was filtered and washed with $CHCl_3$ (50 mL) followed by water (50 mL) and dried to yield **3f** (0.31 g, 92%). Temperature for onset of decomposition: 273 °C. IR (KBr): $\tilde{\nu}$ = 2206 cm^{-1} (C≡C). ^1H NMR (CD_3COCD_3): δ = 8.83 (s, 4 H), 8.54 (s, 2 H), 7.99 (d, *J* = 8.2 Hz, 8 H), 7.84 (d, *J* = 8.2 Hz, 8 H). MALDI-TOF MS: *m*/*z* (%) = 874 (100) [M^+], 875 (80) [M^+ + 1]. HRMS (EI, 70 eV): calcd. for $C_{52}H_{22}F_{12}$ 874.15298; found 874.15250.

1,3,6,8-Tetraethynylpyrene (3g): A red orange solution of **3a** (0.5 g, 0.85 mmol) in degassed THF (30 mL) was treated with *n*Bu_4NF (26 mg, 0.085 mmol) and the resulting mixture was stirred at 30–35 °C for 1 h. The reaction mixture was then poured into ice cold water (100 mL) and the solid obtained was filtered, washed with water (2 × 100 mL), and dried to yield **3g** (0.24 g, 93%) as a pale-yellow solid. Temperature for onset of decomposition: 350 °C. IR (KBr): $\tilde{\nu}$ = 3280, 2099 cm^{-1} (C≡C). ^1H NMR ([D_8]THF): δ = 8.68 (s, 4 H), 8.34 (s, 2 H), 4.28 (s, 4 H) ppm. ^{13}C NMR ([D_8]THF): δ = 135.5, 132.6, 127.6, 123.5, 119.2, 86.1, 81.7 ppm. MS (EI, 70 eV): *m*/*z* (%) = 298 (45) [M^+], 274 (100). HRMS: calcd. for $C_{24}H_{10}$ 298.07825; found 298.07687.

1,3,6,8-Tetrakis{[2-(trimethylsilylethynyl)phenyl]ethynyl}pyrene (5): 1-Bromo-2-(trimethylsilylethynyl)benzene (**4**)[13] (4.58 g, 18.1 mmol) and tetraethynylpyrene **3g** (0.9 g, 3.0 mmol) were stirred at 70 °C for 15 h. The crude product was purified by column chromatography on silica gel using 10% ethyl acetate/hexane (v/v) as the eluent. The product **5** was obtained as a dark-red solid (0.3 g, 10%). IR (KBr): $\tilde{\nu}$ = 2156 cm^{-1} (C≡C). ^1H NMR ($CDCl_3$): δ = 8.91 (s, 4 H), 8.53 (s, 2 H), 7.71–7.59 (m, 8 H), 7.40–7.32 (m, 8 H), 0.29 (s, 18 H), 0.05 (s, 18 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 137.8, 132.7, 131.9, 129.7, 129.0, 128.6, 128.3, 127.4, 125.8, 125.2, 119.0, 103.6, 99.2, 94.8, 91.5, 1.0, 0.1 ppm. MALDI-TOF MS: *m*/*z* = 986 [M^+], 971 [M^+ – Me].

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