

Synthesis and Solvatochromic Behavior of Pyrene Derivatives with 4-Hydroxyphenyl and 4-Hydroxyphenylethynyl Groups

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1-(4-Methoxyphenyl)pyrene (PyrPhOMe(1)), 1,3,6,8-tetrakis(4-methoxyphenyl)pyrene (PyrPhOMe(4)), 1-(4-methoxyphenylethynyl)pyrene (PyrC≡CPhOMe(1)), 1,3,6,8-tetrakis(4-methoxyphenylethynyl)pyrene (PyrC≡CPhOMe(4)), 1-(4-hydroxyphenylethynyl)pyrene (PyrC≡CPhOH(1)), and 1,3,6,8-tetrakis(4-hydroxyphenylethynyl)pyrene (PyrC≡CPhOH(4)) were synthesized via organometallic complex catalysis. Deprotection of the methoxy groups of PyrPhOMe(1) and PyrPhOMe(4) was conducted by treatment with BBr_3. Deprotonation of the OH groups of PyrPhOH(1), PyrPhOH(4), PyrC≡CPhOH(1), and PyrC≡CPhOH(4) through treatment with NaH caused a bathochromic shift in the absorption and photoluminescence (PL) peaks. The bathochromic shift of the deprotonated species increased with the donor number (DN) of the solvents. These observations can be explained as the consequence of intramolecular charge transfer (ICT) from the ONa groups to the pyrene core.

Oligo(*p*-phenylene)s (OPs) are an important class of π-conjugated oligomer because they are useful as luminophores for light-emitting materials,[1–6] as semiconductors for field-effect transistors,[7] as rigid-rod cores for liquid crystalline materials,[8–10] and as amphiphilic materials for biological applications.[11–17] We have recently reported on OPs with an OH group located at either one end or at both ends, namely, OP(*n*)–OH (where *n* is the number of benzene rings; $n = 3$–5) and HO–ArPh(*n*)–OH species (Ar: 9,9-dihexylfluorene-2,7-diyl and 2,5-dioctyloxybenzene-1,4-diyl), respectively.[18,19] These OP(*n*)–OH and HO–ArPh(*n*)–OH compounds exhibited significant solvatochromism where deprotonation of the OH groups, when treated with NaH, caused bathochromic shifts of λ_{max} and λ_{em} that increased with the DN of the solvent. The solvatochromism exhibited by OP(*n*)–ONa and NaO–ArPh(*n*)–ONa was attributed to an intramolecular charge transfer (ICT) from the ONa group(s) to the adjacent rings.[19,20] The degree of bathochromic shift in the deprotonated species increased with an increase in the chain length that corresponds to the expansion of the π-conjugation system. Thus, Ph–ONa substituted by a fused aromatic ring with a large π-conjugation system will exhibit significant bathochromic behavior.

Pyrene derivatives (Pyrs) are an important class of fused aromatic compound in materials science because they can be useful materials for electroluminescence and photovoltaic devices.[20–24] Pyrs are also used as luminescent probes for sensing of biomolecules.[25–28] In this study, the optical properties of Pyrs with 4-hydroxyphenyl groups (PyrPhOHs) were investigated before and after deprotonation of the OH groups. The π-conjugated system of the PyrPhOHs is somewhat restricted by the presence of steric hindrance between the phenyl and Pyr rings. We herein therefore also studied PyrC≡CPhOHs which have ethynyl spacing groups, and subsequently investigated their solvatochromic behavior. It has been reported that Pyrs with arylethynyl groups (PyrC≡CArs) exhibit unique optical properties such as two-photon absorption and electrogenerated chemiluminescence.[29–32] These properties are based on the fact that PyrC≡CArs have a more extended coplanar structure, which thus enables extended π-conjugation and improves their carrier mobilities compared to Pyr–Ars. The large carrier mobility in PyrC≡CPhONa is suited to the development of new solvatochromic materials based on ICT. The investigation into the optical properties of PyrPhOHs and PyrC≡CPhOHs will afford information pertinent to the development of new solvatochromic materials. It is noteworthy that PyrPhOHs and PyrC≡CPhOHs are expected to be useful starting materials for the synthesis of new Pyrs through reactions using the OH groups.

We herein report on the synthesis of Pyrs with 4-hydroxyphenyl and 4-hydroxyphenylethynyl and their optical properties before and after the deprotonation of the OH groups.

Results and Discussion

Synthesis and Characterization. Pyr derivatives with 4-methoxyphenyl, 4-hydroxyphenyl, 4-methoxyphenylethynyl, and 4-hydroxyphenylethynyl groups were synthesized by the methods shown in Scheme 1. The Suzuki coupling reaction of 4-methoxyphenylboronic acid with 1-bromopyrene and 1,3,6,8-tetrabromopyrene yielded 1-(4-methoxyphenyl)pyrene (PyrPhOMe(1)) and 1,3,6,8-tetrakis(4-methoxyphenyl)pyrene (PyrPhOMe(4)), respectively (Scheme 1a). The deprotection of the OMe groups of PyrPhOMe(1) and PyrPhOMe(4) with BBr_3 resulted in the production of PyrPhOH(1) and PyrPhOH(4), respectively. The Sonogashira coupling reaction of 4-ethynylanisole with 1-bromopyrene and 1,3,6,8-tetrabromopyrene yielded 1-(4-methoxyphenylethynyl)pyrene (PyrC≡CPhOMe(1)) and 1,3,6,8-tetrakis(4-methoxyphenylethynyl)-pyrene (PyrC≡CPhOMe(4)), respectively (Scheme 1b). How-

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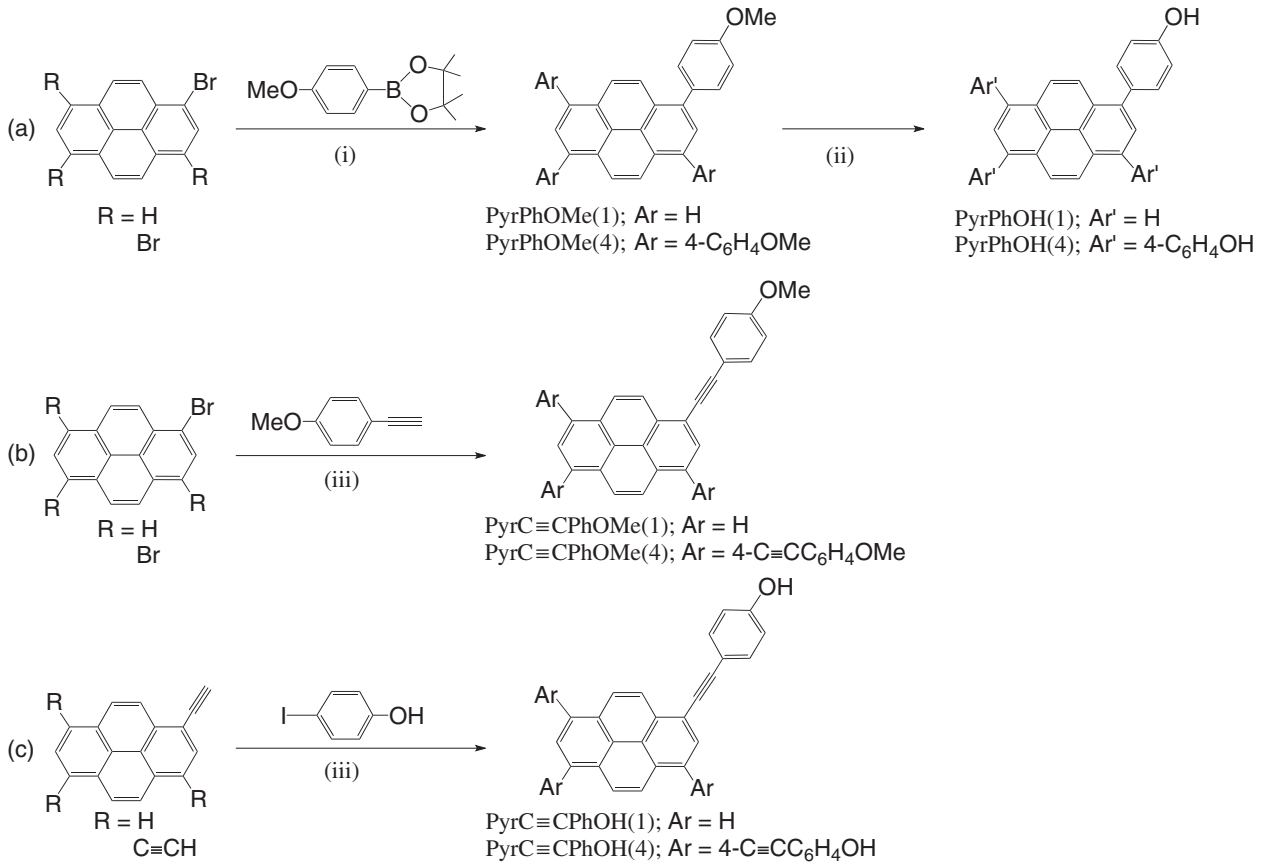

Scheme 1. Synthesis of Pyr derivatives. i) $[Pd(PPh_3)_4]$, K_2CO_3(aq), reflux, THF; ii) BBr_3, CH_2Cl_2, 20 °C, 30 h; iii) $[PdCl_2(PPh_3)_2]$, CuI, NEt_3, rt.

ever, PyrC≡CPhOMe(1) and PyrC≡CPhOMe(4) could not be deprotected by using BBr_3; hence, PyrC≡CPhOH(1) and PyrC≡CPhOH(4) were synthesized by the reaction of 4-iodophenol with 1-bromopyrene and 1,3,6,8-tetrabromopyrene, respectively (Scheme 1c).

The structures of the newly synthesized compounds were determined by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. The solubilities of the obtained compounds are summarized in Table S1. PyrPhOMe(1), PyrPhOMe(4), PyrPhOH(1), PyrC≡CPhOMe(1), and PyrC≡CPhOMe(4) were soluble in polar organic solvents such as 1,4-dioxane, tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) as well as in less polar organic solvents such as chloroform and dichloromethane. However, PyrPhOH(4) and PyrC≡CPhOH(4) were partly soluble in DMF and DMSO but insoluble in dichloromethane and chloroform because of the presence of four hydrophilic OH groups.

^{1}H NMR and IR Spectra. Figure 1 shows the ^{1}H NMR spectra of PyrPhOMe(1), PyrPhOH(1), PyrC≡CPhOMe(1), and PyrC≡CPhOH(1). The ^{1}H NMR spectra of PyrPhOMe(1) and PyrC≡CPhOMe(1) exhibited a peak corresponding to the methoxy groups at δ 3.94 and 3.88, respectively. These peaks disappeared in the ^{1}H NMR spectra of the corresponding demethylated species, thus suggesting that the deprotection reaction proceeded to completion. The electron-withdrawing ethynyl groups on the pyrene and phenylene protons caused the peaks due to the H-atoms at the 10-position of the pyrene ring and the 3-position of the benzene ring of PyrC≡CPhOMe(1) to be observed at lower magnetic field positions than those of PyrPhOMe(1).

The IR spectra of PyrPhOMe(4), PyrPhOH(4), PyrC≡CPhOMe(4), and PyrC≡CPhOH(4) are shown in Figure S1. The main features of the IR spectra of PyrPhOMe(1) and PyrPhOMe(4) were identical, with absorption peaks resulting from C–O stretching, the presence of a phenyl ring, and out-of-plane C–H bending vibrations of *p*-phenylene observed at approximately 1241, 1519, and 839 cm^{-1}, respectively. Similarly, the main features of the IR spectra of PyrC≡CPhOMe(1) and PyrC≡CPhOMe(4) were identical, with the absorption peaks resulting from C≡C and C–O stretching, the presence of a phenyl ring, and out-of-plane C–H bending vibrations of *p*-phenylene observed at approximately 2200, 1246, 1512, and 833 cm^{-1}, respectively. The observation of a broad absorption due to the OH group at 3341 cm^{-1} and disappearance of absorption peaks due to C–O stretching and C–H stretching vibrations of the methoxy group in the IR spectrum of PyrPhOH(4) confirmed occurrence of the deprotection reaction.

Deprotonation of the OH groups of PyrPhOH(1), PyrPhOH(4), PyrC≡CPhOH(1), and PyrC≡CPhOH(4) was carried out through treatment with an excess amount of NaH in DMSO-d_6. The result is that the signal corresponding to the OH group disappeared from the ^{1}H NMR spectra for solutions of these compounds in the presence of NaH, indicating that the deprotonation proceeded quantitatively.

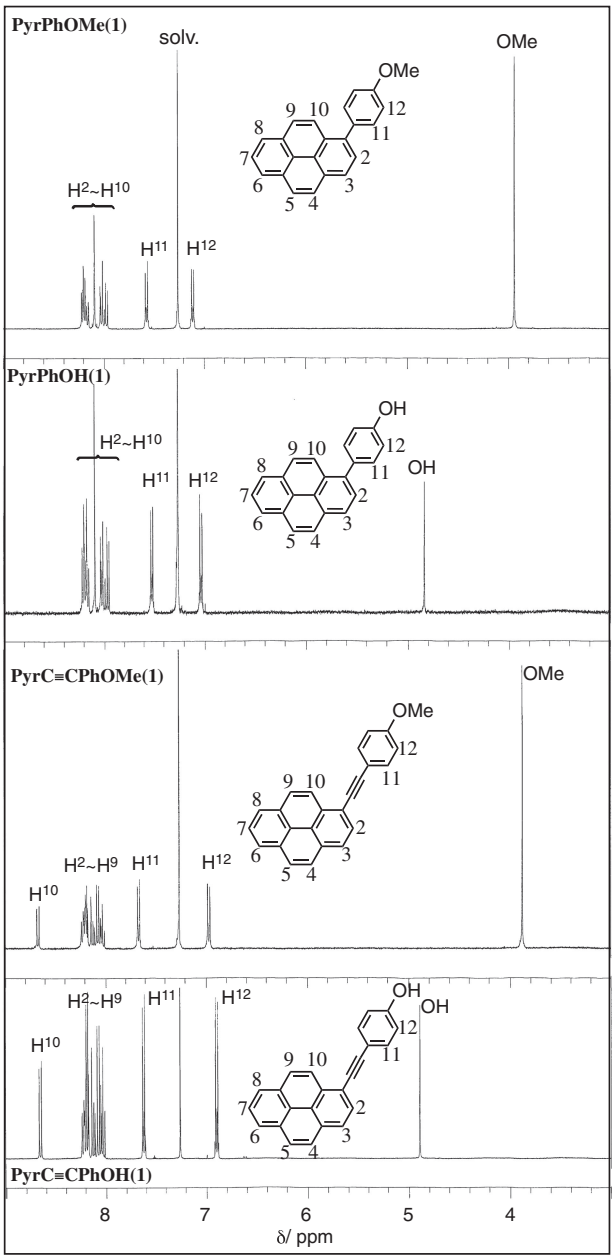

Figure 1. ^{1}H NMR spectra of PyrPhOMe(1), PyrPhOH(1), PyrC≡CPhOMe(1), and PyrC≡CPhOH(1) in $CDCl_3$.

UV–vis Spectra. The optical data of the pyrene derivatives obtained in this study are summarized in Tables 1–4. The UV–vis spectra of the pyrene derivatives can be divided into three distinguishable parts. These three regions appear to be separate states of electronic transition, as shown in Figure 2.

Figure 3 shows the UV–vis spectra of PyrPhOMe(1), PyrC≡CPhOMe(1), PyrPhOMe(4), and PyrC≡CPhOMe(4) in dichloromethane. The absorption peaks in the ranges of 240–260, 275–360, and 340–490 nm in the UV–vis spectra of the compounds are probably results of the electronic transitions directed along the *y*, *x*, *z* axes, respectively, as shown in Figure 2. The absorption wavelengths (λ_z's) due to the electronic transitions directed along the *z* axis of PyrC≡CPhOMe(1) and PyrC≡CPhOMe(4) are longer than those of PyrPhOMe(1) and PyrPhOMe(4) because of the presence of the ethynyl spacing groups in PyrC≡CPhOMe(1) and PyrC≡CPhOMe(4) which reduces the bond twisting between the pyrene and benzene rings. Whereas the absorption wavelengths due to the electronic transition directed along the *y* axis of PyrC≡CPhOMe(1) and PyrC≡CPhOMe(4) are comparable to those of PyrPhOMe(1) and PyrPhOMe(4). The absorption peaks of PyrPhOMe(4), PyrPhOH(4), PyrC≡CPhOMe(4), and PyrC≡CPhOH(4) are observed at longer wavelengths than those of PyrPhOMe(1), PyrPhOH(1), PyrC≡CPhOMe(1), and PyrC≡CPhOH(1), respectively. This observation is attributed to the fact that the π-conjugated system of the tetrasubstituted compounds is larger than that of the monosubstituted compounds because of the presence of the ethynyl spacing group.

PyrC≡CPhOMe(1) and PyrC≡CPhOMe(4) exhibit two couples of absorption peaks at approximately 370 and 390 nm and 460 and 490 nm due to the electronic transition directed along the *z* axis, respectively. The two couples of absorption peaks can be assigned to the C–C stretching modes of vibration of the ground electronic state of the pyrene moiety. Two similar couples of absorption peaks are observed in the UV–vis spectra of pyrene and pyrenes with arylethynyl substituent(s).[31] The disappearance of coupled absorption peaks in PyrPhOMe(1) and PyrPhOMe(4) is ascribed to the assumption that the hydroxyphenyl group bonded to the pyrene core affects the C–C stretching vibration of the pyrene core because of the presence of steric hindrance between the 4-hydroxyphenyl group and the pyrene core. The ethynyl spacing group of PyrC≡CPhOMe(1) and PyrC≡CPhOMe(4) reduces the steric hindrance between the hydroxyphenyl group and the pyrene core, which enables the C–C stretching of the pyrene moiety in the ground electronic state.

Figure 4 shows the UV–vis spectra of PyrPhOH(1), PyrPhOH(4), PyrC≡CPhOH(1), and PyrC≡CPhOH(4) before and after the treatment with NaH in DMF. The treatment of the DMF solutions of PyrPhOH(1), PyrPhOH(4), PyrC≡CPhOH(1), and PyrC≡CPhOH(4) with NaH causes a bathochromic shift in absorption bands. The formation of PyrPhONa(1), PyrPhONa(4), PyrC≡CPhONa(1), and PyrC≡CPhONa(4) was mainly responsible for the shift in absorption toward a longer wavelength. To prove that these observations were due to the deprotonation of the OH groups after treatment with NaH, we confirmed that there was no change in the absorption spectra of the compounds with the OMe groups upon the addition of NaH. The degree of bathochromic shift ($\Delta\lambda$) in the peak that corresponds to the electric transition along the *z* axis was the largest of the three described. This result suggests that ICT from the ONa group to the pyrene core was preferred through the benzene and phenylethynyl groups. The $\Delta\lambda$ values for PyrC≡CPhONa(1) and PyrC≡CPhONa(4) were larger than those for PyrPhONa(1) and PyrPhONa(4). These results correspond to the assumption that the ICT from the ONa group to the pyrene core occurred more easily in PyrC≡CPhONa(1) and PyrC≡CPhONa(4) because of less steric hindrance between the PhONa group and the pyrene core.

The bathochromic shift attributable to deprotonation is dependent on the DN of the solvent used. As shown in Figure 5, the λ_z values for PyrPhOH(1), PyrPhOH(4), PyrC≡CPhOH(1), PyrC≡CPhOH(4), and their deprotonated species shifted to longer wavelengths as the DN of the solvent was

Table 1. Optical Data of PyrPhOMe(1), PyrPhOH(1), and PyrPhONa(1)

	DN[a]	PyrPhOMe(1)		PyrPhOH(1)		PyrPhONa(1)	
		Absorption/nm[b]	Emission/nm[c]	Absorption/nm[b]	Emission/nm[c]	Absorption/nm[b]	Emission/nm[c]
CH_2Cl_2	0	245 (4.62), 280 (4.48), 345 (4.48)	389, 406 (349)	245 (4.72), 280 (4.64), 345 (4.50)	389, 406 (350)	240, 349	489 (378)
1,4-dioxane	14.8	246 (4.70), 278 (4.48), 344 (4.45)	388, 405 (349)	212 (4.31), 245 (4.53), 278 (4.56), 345 (4.21)	392, 406 (348)	219, 271, 346	488 (378)
THF	20	278 (4.65), 344 (4.57)	389, 406 (347)	244 (4.76), 278 (4.66), 345 (4.28)	392, 404[d] (348)	244, 268, 373	501 (373)
DMF	26.6	280 (4.45), 345 (4.45)	405 (352)	273 (4.48), 278 (4.50), 347 (4.34)	409 (351)	275, 341, 441	—[e]
DMSO	29.8	280 (4.59), 348 (4.45)	392[d], 406 (349)	281, 349 (4.24)	411 (353)	278, 337, 443	—[e]

a) DN: Donor number. b) $\log \varepsilon$ values are shown in the parenthesis. c) Excitation wavelengths are shown in parenthesis. d) Shoulder peak. e) Not observed.

Table 2. Optical Data of PyrPhOMe(4), PyrPhOH(4), and PyrPhONa(4)

	DN[a]	PyrPhOMe(4)		PyrPhOH(4)		PyrPhONa(4)	
		Absorption/nm[b]	Emission/nm[c]	Absorption/nm[b]	Emission/nm[c]	Absorption/nm[b]	Emission/nm[c]
CH_2Cl_2	0	269, 393	432 (393)	—[d]	—[d]	—[d]	—[d]
1,4-dioxane	14.8	263, 301, 391	430 (391)	313, 396	430 (382)	272, 378, 424	506 (378)
THF	20	258, 304, 393	431 (393)	306, 393	432 (384)	270, 443	497 (363)
DMF	26.6	273, 397	436 (397)	272, 399	438 (389)	274, 376, 484	551 (376)
DMSO	29.8	273, 399	439 (399)	275, 403	442 (395)	369, 490	549 (370)

a) DN: Donor number. b) $\log \varepsilon$ value was not estimated due to low solubility. c) Excitation wavelengths are shown in parenthesis. d) Not measured due to low solubility.

Table 3. Optical Data of PyrC≡CPhOMe(1), PyrC≡CPhOH(1), and PyrC≡CPhONa(1)

	DN[a]	PyrC≡CPhOMe(1)		PyrC≡CPhOH(1)		PyrC≡CPhONa(1)	
		Absorption/nm[b]	Emission/nm[d]	Absorption/nm[b]	Emission/nm[d]	Absorption/nm[b]	Emission/nm[d]
CH_2Cl_2	0	285 (5.24), 299 (4.91)[c], 351 (4.49), 366 (4.72), 390 (4.70)	405, 409[c]	285 (4.58), 297 (4.58), 348 (4.46)[c], 366 (4.69), 388 (4.67)	401, 410 (366)	286 (4.19), 297 (4.20), 367 (4.30), 388 (4.29)	506 (410)
1,4-dioxane	14.8	285 (5.29), 299 (4.95)[c], 349 (4.46), 366 (4.68), 390 (4.64)	400, 419	285 (4.60), 298 (4.52), 351 (4.46)[c], 366 (4.69), 389 (4.64)	402, 414 (366)	284 (4.47), 322 (4.34), 344 (4.22), 393 (4.38), 422 (4.44)	522 (422)
THF	20	284 (4.77), 298 (4.66), 352 (4.43)[c], 366 (4.66), 389 (4.63)	402, 409[c]	285 (4.55), 299 (4.45), 352 (4.40)[c], 367 (4.63), 389 (4.60)	409 (367)	283 (4.58), 389 (4.39), 437 (4.31)	545 (447)
DMF	26.6	286 (5.08), 299 (4.91), 353 (4.52)[c], 368 (4.76), 390 (4.75)	413, 418[c]	286 (4.77), 298 (4.64), 355 (4.48)[c], 369 (4.72), 391 (4.69)	430 (369)	281 (4.98), 338 (4.67), 390 (4.22), 479 (4.53)	—[e]
DMSO	29.8	286 (4.77), 300 (4.65), 352 (4.44)[c], 372 (4.68), 394 (4.68)	421	287 (4.53), 301 (4.43), 355 (4.33)[c], 370 (4.60), 394 (4.56)	439 (370)	282 (4.56), 338 (4.43), 494 (4.41)	—[e]

a) DN: Donor number. b) $\log \varepsilon$ values are shown in the parenthesis. c) Shoulder peak. d) Excitation wavelengths are shown in parenthesis. e) Not observed.

increased. In contrast to the small bathochromic shift for PyrPhOH(1), PyrPhOH(4), PyrC≡CPhOH(1), and PyrC≡CPhOH(4), with an increase in the DN of the solvent, the λ_z values of PyrPhONa(1), PyrPhONa(4), PyrC≡CPhONa(1), and PyrC≡CPhONa(4) were larger than those of PyrPhOH(1), PyrPhOH(4), PyrC≡CPhOH(1), and PyrC≡CPhOH(4). For example, the λ_z values of PyrPhONa(1) and PyrPhONa(4) vary from 349 and 424 nm in 1,4-dioxane (DN = 14.8) to 443 and 490 nm in DMSO (DN = 29.8), through to values of 373 and 443 nm in THF (DN = 20.0), respectively. Similarly, those of PyrC≡CPhONa(1) and PyrC≡CPhONa(4) vary from 422 and 501 nm 1,4-dioxane (DN = 14.8) to 494 and 610 nm in DMSO (DN = 29.8). The large $\Delta\lambda$ values can be attributed to the fact that solvents with a high DN effectively solvate with Na^+ to stabilize the deprotonated species in the solutions. Similar solvatochromic behavior was observed in the cases of OP(n)–OH ($n = 4$ and 5) and OP(n)–ONa ($n = 4$ and 5), as reported earlier.[18,19] The fact that the $\Delta\lambda$ values for PyrC≡CPhONa(1) and PyrC≡CPhONa(4) were larger than those for PyrPhONa(1) and PyrPhONa(4) corresponds to the increased length of π-

Table 4. Optical Data of PyrC≡CPhOMe(4), PyrC≡CPhOH(4), and PyrC≡CPhONa(4)

	DN[a)]	PyrC≡CPhOMe(4)		PyrC≡CPhOH(4)		PyrC≡CPhONa(4)	
		Absorption/nm[b)]	Emission/nm[c)]	Absorption/nm[b)]	Emission/nm[c)]	Absorption/nm[b)]	Emission/nm[c)]
CH_2Cl_2	0	254, 352, 451, 482	497, 529 (355)	—[d)]	—[d)]	—[d)]	—[d)]
1,4-dioxane	14.8	351, 449, 477	493, 526 (354)	255, 350, 449, 476	493, 526 (356)	283, 398, 501	589 (403)
THF	20	262, 354, 451, 478	495, 527 (356)	257, 355, 452, 480	497, 530 (355)	273, 414, 496, 554	599 (404)
DMF	26.6	268, 355, 455, 482	501, 533 (359)	268, 340, 456, 485	505, 537 (358)	338, 448, 523, 599	595 (447)
DMSO	29.8	262, 359, 458, 487	505, 538 (362)	264, 363, 456, 490	511, 541 (365)	296, 451, 535, 610	—[e)]

a) DN: Donor number. b) log ε value was not estimated due to low solubility. c) Excitation wavelengths are shown in parenthesis. d) Not measured due to low solubility. e) Not observed.

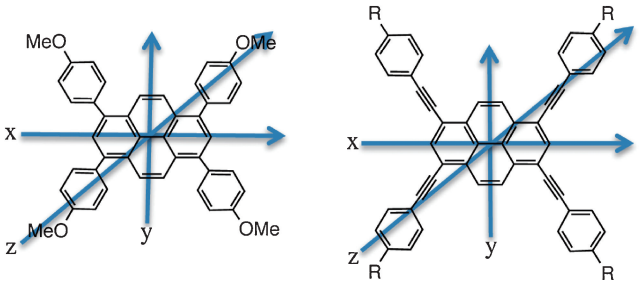

Figure 2. Electronic transition directions in pyrene derivatives.

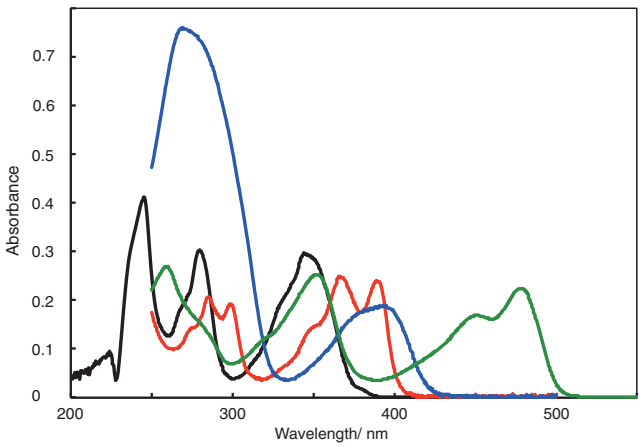

Figure 3. UV–vis spectra of the dichloromethane solutions of PyrPhOMe(1) (black curve), PyrC≡CPhOMe(1) (red curve), PyrPhOMe(4) (blue curve), and PyrC≡CPhOMe(4) (green curve).

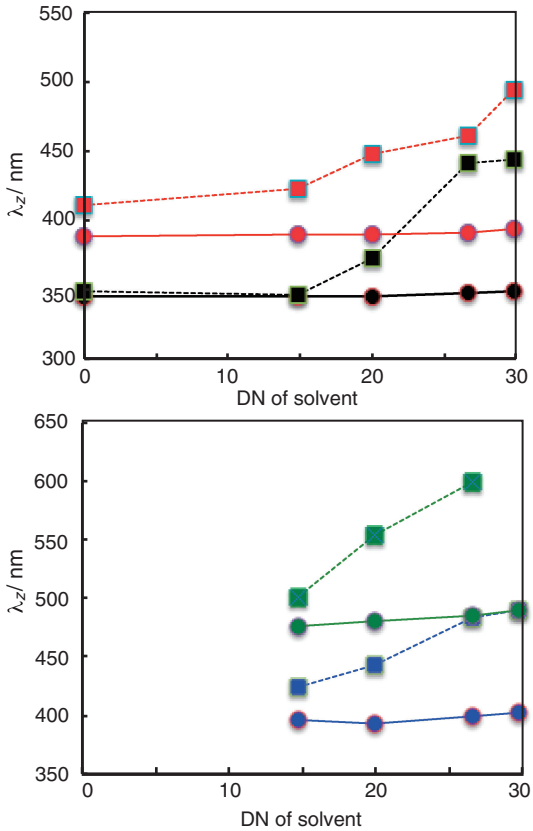

Figure 4. Dependence of λ_z of PyrPhOH(1) (black line), PyrPhONa(1) (black dashed line), PyrC≡CPhOH(1) (red line), PyrC≡CPhONa(1) (red dashed line), PyrPhOH(4) (blue line), PyrPhONa(4) (blue dashed line), PyrC≡CPhOH(4) (green line), and PyrC≡CPhONa(4) (green dashed line) on the DNs of solvents.

conjugation in PyrC≡CPhONa(1) and PyrC≡CPhONa(4) that arises from the presence of the ethynyl spacing groups.

Photoluminescence Spectra. The compounds obtained in this study and their deprotonated species are photoluminescent in solution. Figure 6 shows the photoluminescence (PL) spectra of PyrPhOH(1), PyrPhOH(4), PyrC≡CPhOH(1), PyrC≡CPhOH(4), and their deprotonated species in THF. The PL data are summarized in Tables 1–4. The observation that the PL peak positions for PyrPhOH(4) and PyrC≡CPhOH(4) were longer than those for PyrPhOH(1) and PyrC≡CPhOH(1) is comparable to the result that the λ_{max} wavelengths for PyrPhOH(4) and PyrC≡CPhOH(4) were longer than those for PyrPhOH(1) and PyrC≡CPhOH(1).

The PL peak positions for PyrPhOH(1), PyrPhOH(4), PyrC≡CPhOH(1), and PyrC≡CPhOH(4) shifted to longer wavelengths after deprotonation with NaH. This shift is comparable to the bathochromic shift observed in the UV–vis spectra of these compounds. The emission peak positions for PyrPhOH(1), PyrPhOH(4), PyrC≡CPhOH(1), PyrC≡CPhOH(4), and their deprotonated species depended on the DN of the solvent; therefore, the emission color can be tuned by changing the solvent. For example, PyrPhONa(4) exhibited blue, green, and yellow emissions after it was irradiated with UV light in 1,4-dioxane (DN = 14.8), THF (DN = 20.0), and DMF (DN = 26.6), respectively, as shown in Figure 7.

As shown in Figure 8, by varying solvents such as CH_2Cl_2 and 1,4-dioxane, which have small DN values, with those such as DMF and DMSO, which have large DN values, it is observed

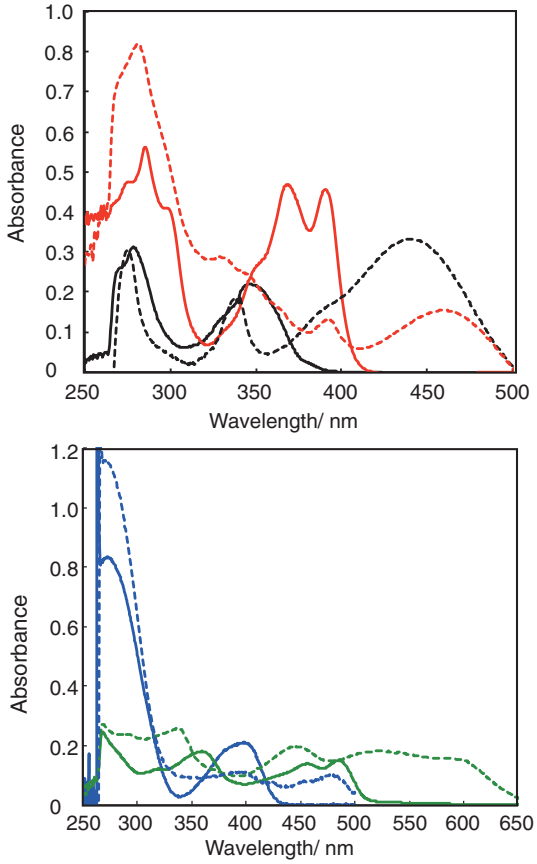

Figure 5. UV–vis spectra of PyrPhOH(1) (black curve), PyrPhONa(1) (black dashed curve), PyrC≡CPhOH(1) (red curve), PyrC≡CPhONa(1) (red dashed curve), PyrPhOH(4) (blue curve), PyrPhONa(4) (blue dashed curve), PyrC≡CPhOH(4) (green curve), and PyrC≡CPhOH(4) (green dashed curve) in DMF.

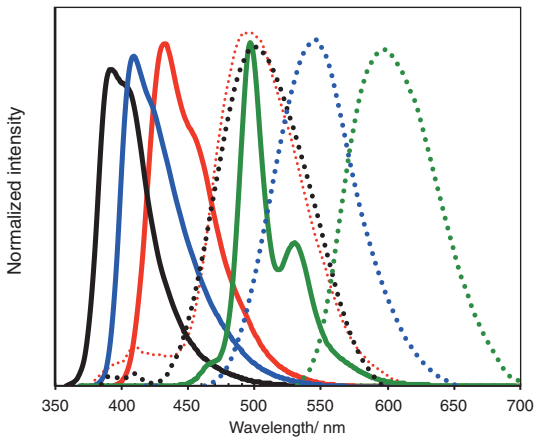

Figure 6. PL spectra of PyrPhOH(1) (black solid curve), PyrPhOH(4) (red solid curve), PyrC≡CPhOH(1) (blue solid curve), PyrC≡CPhOH(4) (green solid curve), and their deprotonated species (respective dashed curve) in THF.

that the emission peak positions for PyrPhOH(1), PyrPhOH(4), PyrC≡CPhOH(1), and PyrC≡CPhOH(4) shift by only 4–29 nm. However, a significantly large shift in the emission

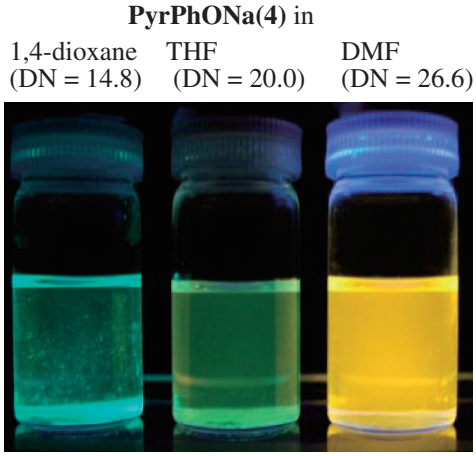

Figure 7. Photographs of PyrPhONa(4) when it was irradiated with UV light in 1,4-dioxane (DN = 14.8), THF (DN = 20.0), and DMF (DN = 26.6).

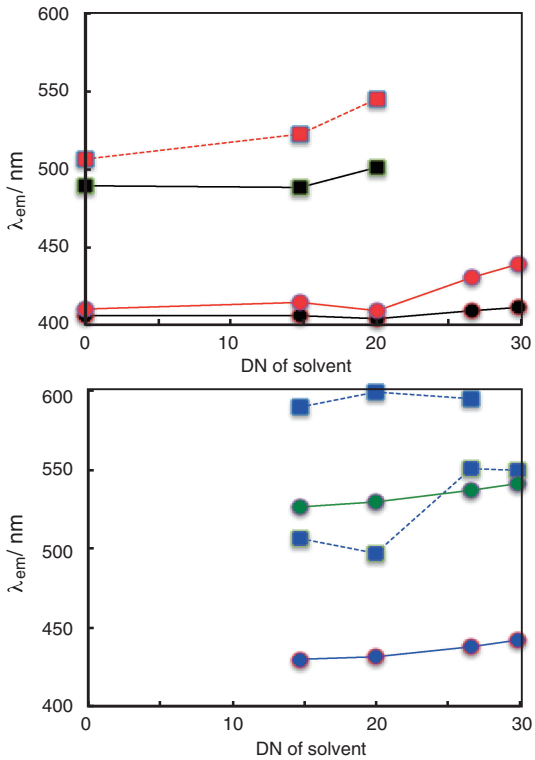

Figure 8. Dependence of λ_{em} of PyrPhOH(1) (black line), PyrPhONa(1) (black dashed line), PyrC≡CPhOH(1) (red line), PyrC≡CPhONa(1) (red dashed line), PyrPhOH(4) (blue line), PyrPhONa(4) (blue dashed line), PyrC≡CPhOH(4) (green line), and PyrC≡CPhONa(4) (green dashed line) on the DNs of solvents. When two emission peaks were observed, the longer wavelength was adopted for the data point.

peaks for PyrPhONa(1), PyrPhONa(4), PyrC≡CPhONa(1), and PyrC≡CPhONa(4) occurred as the DN of the solvent was increased. These observations are consistent with the observation that with an increase in the DN of the solvent, λ_{max} of PyrPhONa(1), PyrPhONa(4), PyrC≡CPhONa(1), and PyrC≡CPhONa(4) in solution shifts to a longer wavelength than that

of PyrPhOH(1), PyrPhOH(4), PyrC≡CPhOH(1), and PyrC≡CPhOH(4). The remarkable solvatochromic shift of the PL peak position of PyrPhONa(1), PyrPhONa(4), PyrC≡CPhONa(1), and PyrC≡CPhONa(4) may be due to the shift in charge from the phenolate group to the adjacent rings. In addition to the effect of charge shift, a large amount of stabilization energy produced by the solvation of PyrPhONa(1), PyrPhONa(4), PyrC≡CPhONa(1), and PyrC≡CPhONa(4) may contribute to the solvatochromic red shift as the DN of the solvent is increased. There was no change in the PL spectra of PyrPhOMe(1), PyrPhOMe(4), PyrC≡CPhOMe(1), and PyrC≡CPhOMe(4) upon the addition of NaH, which suggests that the solvatochromism in PyrPhONa(1), PyrPhONa(4), PyrC≡CPhONa(1), and PyrC≡CPhONa(4) can be attributed to the deprotonation of the OH group after treatment with NaH.

The quantum yields of the PLs of the THF solutions of PyrPhOH(1), PyrPhOH(4), PyrC≡CPhOH(1), and PyrC≡CPhOH(4) were 19, 38, 43, and 31%, respectively, while those of PyrPhONa(1), PyrPhONa(4), PyrC≡CPhONa(1), and PyrC≡CPhONa(4) were 0.02, 3, 0.1, and 0.01%, respectively. The fact that the quantum yields of the PLs of PyrPhONa(1), PyrPhONa(4), PyrC≡CPhONa(1), and PyrC≡CPhONa(4) are lower than those of PyrPhOH(1), PyrPhOH(4), PyrC≡CPhOH(1), and PyrC≡CPhOH(4) is attributed to the ICT in PyrPhONa(1), PyrPhONa(4), PyrC≡CPhONa(1), and PyrC≡CPhONa(4). It has been reported that the ICT in π-conjugated molecules reduces their PL emission efficiencies.[7]

Conclusion

Pyrene derivatives with 4-hydroxyphenyl and 4-hydroxyphenylethynyl groups were obtained by using reactions with transition-metal complexes. The treatment of these compounds with a base produced corresponding deprotonated species, whose absorption and PL peak positions in solution shifted toward longer wavelengths with an increase in the DN of the solvent. The optical properties of the pyrene derivatives were significantly affected by bond twisting between the 4-hydroxyphenyl group and the central pyrene core. The introduction of an ethynyl spacing group between the 4-hydroxyphenyl group and the pyrene core enhanced its solvatochromic behavior. The results obtained in this study will be useful in providing information for the development of new solvatochromic materials.

Experimental

General. Solvents were dried, distilled, and stored under nitrogen. 1-Ethynylpyrene and 1,3,6,8-tetraethynylpyrene were synthesized according to the literature.[31,32] Other reagents were purchased and used without further purification. Reactions were carried out with standard Schlenk techniques under nitrogen.

IR and NMR spectra were recorded on a JASCO FT/IR-660 PLUS spectrophotometer and JEOL AL-400 and ECX-500 spectrometers, respectively. Elemental analysis was performed on a Yanagimoto MT-5 CHN corder. UV–vis and PL spectra were obtained with a JASCO V-560 spectrometer and a JASCO FP-6200 spectrofluorometer, respectively. Quantum yields were calculated by using a diluted ethanol solution of 7-dimethylamino-4-methylcoumarin as the standard.

Synthesis. PyrPhOMe(1): 4-Methoxyphenylboronic acid (0.79 g, 5.2 mmol) and 1-bromopyrene (1.40 g, 5.0 mmol) were dissolved in 20 mL of dry toluene under N_2. To the solution were added K_2CO_3(aq) (2.0 M, 10 mL; N_2 bubbled before use), $[Pd(PPh_3)_4]$ (0.30 g, 0.26 mmol), and several drops of the phase-transfer catalyst (Aliquat336). After the mixture was refluxed for 48 h, the precipitate from the reaction solution was removed by filtration, and the filtrate was extracted with chloroform and washed with brine. The solvent was removed under vacuum to give a light yellow solid, which was purified by silica gel column chromatography (eluent: $CHCl_3$/hexane; v/v = 3/2). The solvent was removed by evaporation and the resulting solid was dried in vacuo to give PyrPhOMe(1) as a light yellow powder (0.64 g, 42%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22–7.96 (m, 9H), 7.57 (d, J = 8.8 Hz, 2H, H of *m*-position of MeOPh ring), 7.11 (d, J = 8.8 Hz, 2H, H of *o*-position of MeOPh ring), 3.94 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.0, 137.4, 133.5, 131.6, 131.5, 131.0, 130.3, 128.6, 127.7, 127.4, 127.3, 127.2, 125.9, 125.4, 125.0, 124.9, 124.7, 124.6, 113.8, 55.4 (CH_3). IR (KBr, cm^{-1}): 3040, 2996, 2954, 2899, 2832, 1604, 1519, 1497, 1458, 1438, 1283, 1241, 1175, 1105, 1034, 828, 839. Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92%. Found: C, 80.88; H, 6.10%.

Synthesis of PyrPhOMe(4): PyrPhOMe(4) was synthesized by the reaction of 4-methoxyphenylboronic acid with 1,3,6,8-tetrabromopyrene analogously. Yield = 53%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (s, 4H, H at 4,5,9,10-positions of pyrene ring), 7.96 (s, 2H, H at 2,7-positions of pyrene ring), 7.60 (d, J = 8.4 Hz, 8H, H of *m*-position of MeOPh ring), 7.08 (d, J = 8.8 Hz, 8H, H of *o*-position of MeOPh ring), 3.92 (s, 12H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1 (C at 2,7-positions of pyrene ring), 136.8, 131.8 (C of *m*-position of MeOPh ring), 129.7, 128.1, 126.2, 125.2 (C at 4,5,9,10-positions of pyrene ring), 113.9 (C of *o*-position of MeOPh ring), 55.5 (CH_3). IR (KBr, cm^{-1}): 3033, 3000, 2952, 2930, 2833, 1607, 1514, 1495, 1461, 1287, 1247, 1175, 1034, 755. Anal. Calcd for $C_{44}H_{34}O_4$: C, 84.32; H, 5.47%. Found: C, 83.96; H, 5.23%.

PyrC≡CPhOMe(1): 4-Ethynylanisole (0.84 g, 6.4 mmol) and 1-bromopyrene (1.41 g, 5.0 mmol) were dissolved in a mixture of dry toluene (5 mL) and triethylamine (5 mL) under N_2. To the solution were added $[PdCl_2(PPh_3)_2]$ (0.044 g, 0.063 mmol) and CuI (0.017 g, 0.090 mmol). After the reaction solution was stirred at 70 °C for 86 h, the solvent was removed under vacuum to give a light yellow solid, which was purified by silica gel column chromatography (eluent: $CHCl_3$/hexane; v/v = 1/2). The solvent was removed by evaporation and a resulting solid was dried in vacuo to give PyrC≡CPhOMe(1) as a yellow powder (0.59 g, 35%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (d, J = 9.2 Hz, 1H, H at 10-position of pyrene ring), 8.24–8.01 (m, 8H), 7.66 (d, J = 8.8 Hz, 2H, H of *m*-position of MeOPh ring), 6.97 (d, J = 8.8 Hz, 2H, H of *o*-position of MeOPh ring), 3.88 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.8, 133.2, 131.7, 131.3, 131.1, 131.0, 129.4, 128.2, 128.0, 127.3, 126.2, 125.6, 125.51, 125.46, 124.5, 124.4, 118.2, 115.7, 114.2, 95.2 (Pyr*C*≡CPh), 87.4 (PyrC≡*C*Ph), 55.4 (CH_3). IR (KBr, cm^{-1}): 3039, 2958, 2927, 2838, 2202, 1597, 1512, 1450, 1288, 1246, 1176, 1036, 755. Anal. Calcd for $C_{25}H_{16}O$: C, 90.33; H, 4.85%. Found: C, 90.67; H, 5.06%.

PyrC≡CPhOMe(4): PyrC≡CPhOMe(4) was synthesized using a procedure similar to that used for PyrC≡CPhOMe(1).

Yield = 3%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 4H, H at 4,5,9,10-positions of pyrene ring), 8.41 (s, 2H, H at 2,7-positions of pyrene ring), 7.67 (d, $J = 8.8$ Hz, 8H, H of *m*-position of MeOPh ring), 6.98 (d, $J = 8.8$ Hz, 8H, H of *o*-position of MeOPh ring), 3.89 (s, 12H, CH_3). ^{13}C NMR measurement was not acquired due to the low solubility of this compound. IR (KBr, cm^{-1}): 2999, 2934, 2834, 2199, 1595, 1511, 1287, 1248, 1173, 1031, 833. Anal. Calcd for $C_{52}H_{34}O_4 \cdot 0.3H_2O$: C, 85.76; H, 4.79%. Found: C, 85.74; H, 5.00%.

PyrPhOH(1): After a dichloromethane solution (5 mL) of BBr_3 (1.0 mL, 10 mmol) was added dropwise to a dichloromethane solution (20 mL) of PyrPhOMe(1) (0.256 g, 0.83 mmol) at −78 °C, the reaction solution was stirred at 20 °C for 3 h and quenched with KOH(aq) (5 M, 5 mL). The resulting precipitate was removed by filtration, extracted with chloroform, and dried under vacuum to give PyrPhOH(1) as a light brown solid (0.24 g, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22–7.95 (m, 9H), 7.52 (d, $J = 8.8$ Hz, 2H, H of *m*-position of HOPh ring), 7.04 (d, $J = 8.8$ Hz, 2H, H of *o*-position of HOPh ring), 4.83 (s, 1H, OH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.9, 137.4, 133.8, 131.8, 131.5, 131.0, 128.6, 127.7, 127.43, 127.36, 127.29, 126.0, 125.3, 125.03, 125.01, 124.9, 124.8, 124.6, 115.3 (C of *o*-position of HOPh ring). IR (KBr, cm^{-1}): 3244, 3043, 1609, 1523, 1498, 1448, 1434, 848, 837, 758, 721. Anal. Calcd for $C_{22}H_{14}O \cdot 0.2H_2O$: C, 88.68; H, 4.87%. Found: C, 88.57; H, 4.90%.

PyrPhOH(4): PyrPhOH(4) was synthesized using a procedure similar to that used for PyrPhOH(1). Yield = 60%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.65 (s, 4H, OH), 8.12 (s, 4H, H at 4,5,9,10-positions of pyrene ring), 7.85 (s, 2H, H at 2,7-positions of pyrene ring), 7.49 (d, $J = 8.4$ Hz, 8H, H of *m*-position of HOPh ring), 6.98 (d, $J = 8.4$ Hz, 8H, H of *o*-position of HOPh ring). ^{13}C NMR (125 MHz, DMSO-d_6): δ 156.9, 136.8, 131.7, 130.9, 129.5, 127.1, 125.8, 124.8, 115.5 (C of *o*-position of HOPh ring). IR (KBr, cm^{-1}): 3341, 1610, 1516, 1495, 1257, 1229, 1172, 835. Anal. Calcd for $C_{40}H_{26}O_4 \cdot 0.7H_2O$: C, 82.37; H, 4.74%. Found: C, 82.59; H, 4.93%.

PyrC≡CPhOH(1): 1-Ethynylpyrene (0.44 g, 1.9 mmol), 4-iodophenol (0.53 g, 2.4 mmol), [$PdCl_2(PPh_3)_2$] (0.042 g, 0.060 mmol), and CuI (0.024 g, 0.13 mmol) were added to triethylamine (5 mL) at −4 °C. After the suspension was stirred at 20 °C for 24 h, the solvent was removed under vacuum. The resulting solid was purified by silica gel column chromatography (eluent: $CHCl_3$/acetone; v/v = 10/1). The solvent was removed by evaporation and the resulting solid was extracted with hexane. After the solvent was removed under vacuum, the resulting solid was dried under vacuum to give PyrC≡CPhOH(1) as a yellow powder (0.065 g, 11%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (d, $J = 9.2$ Hz, 1H, H at 10-position of pyrene ring), 8.24–8.01 (m, 8H), 7.63 (d, $J = 8.8$ Hz, 2H, H of *m*-position of HOPh ring), 6.91 (d, $J = 8.8$ Hz, 2H, H of *o*-position of HOPh ring), 4.89 (s, 1H, OH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.8, 131.7, 131.3, 131.1, 131.0, 129.5, 128.2, 128.0, 127.3, 126.2, 125.6, 125.52, 125.49, 124.54, 124.52, 124.4, 118.1, 116.0, 115.6, 94.9 (PyrC≡CPh), 87.3 (PyrC≡CPh). IR (KBr, cm^{-1}): 3312, 3035, 2206, 1608, 1587, 1517, 1435, 1362, 838, 822, 714. Anal. Calcd for $C_{24}H_{14}O \cdot 0.1H_2O$: C, 90.03; H, 4.47%. Found: C, 89.81; H, 5.07%.

PyrC≡CPhOH(4): 1,3,6,8-Tetraethynylpyrene (0.16 g, 0.54 mmol), 4-iodophenol (0.87 g, 4.0 mmol), [$PdCl_2(PPh)_2$] (0.051 g, 0.072 mmol), and CuI (0.027 g, 0.14 mmol) were added to triethylamine (8 mL) at −4 °C. After the suspension was stirred at 20 °C for 47 h, the solvent was removed under vacuum. The resulting solid was washed with chloroform and water, collected by filtration, and dried under vacuum to give PyrC≡CPhOH(4) as a yellowish green powder (0.074 g, 21%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.09 (s, 4H, OH), 8.78 (s, 4H, H at 4,5,9,10-positions of pyrene ring), 8.41 (s, 2H, H at 2,7-positions of pyrene ring), 7.66 (d, $J = 8.4$ Hz, 8H, H of *m*-position of HOPh ring), 6.91 (d, $J = 8.8$ Hz, 8H, H of *o*-position of HOPh ring). ^{13}C NMR measurement was not obtained due to the low solubility of this compound. IR (KBr, cm^{-1}): 3389, 3196, 1594, 1512, 1264, 1166, 831. Anal. Calcd for $C_{48}H_{26}O_4 \cdot 0.5H_2O$: C, 85.32; H, 4.03%. Found: C, 85.65; H, 4.42%.

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Supporting Information

Solubilities, IR, ^{1}H, and ^{13}C NMR spectra of the obtained compounds. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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