



Synthesis of oligophenylenes containing hydroxyl group and their solvatochromic behavior

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ABSTRACT

Oligo(*p*-phenylene)s containing hydroxyl group(s), namely, **OPP(*n*)-OH** (*n*=3, 4, and 5; *n* denotes the number of benzene rings), **HO-OPP(3)-OH**, and 1,3,5-tri(4-biphenyl)phenol **TBP-OH** were synthesized in high yields by the Suzuki coupling reaction. Absorption maxima (λ_{max}) of **OPP(*n*)-OHs** shifted progressively toward long wavelengths due to the expansion of the π -conjugation system with an increase in the number of benzene rings. Deprotonation of the OH group of **OPP(*n*)-OHs** by treatment with NaH caused a bathochromic shift of λ_{max} . The bathochromic shift of the deprotonated species increased with the donor numbers (DNs) of the solvents. The emission peak positions of **OPP(*n*)-OH** and **OPP(*n*)-ONa** depended on the DN of the solvents; that is, the emission color could be tuned by changing the solvent.

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1. Introduction

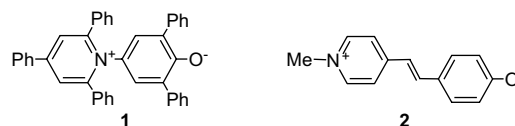
Well-defined conjugated oligomers have attracted considerable attention due to their nondefected structures for the fabrication of electronic and optical devices.¹ They can also be used as model compounds for understanding the chemical and physical properties of related polymeric materials and for investigating structure–property correlation.

Oligo(*p*-phenylene)s (OPPs) are an important class of π -conjugated oligomers because they are useful as luminophores for light-emitting materials,² as semiconductors for field-effect transistors,³ as rigid-rod cores for liquid crystalline materials,⁴ and as amphiphilic materials for biological applications.⁵ Recently, OPPs have been converted into planarized ladder-type materials,⁶ relatively large polycyclic aromatic hydrocarbons,⁷ novel macrocycles,⁸ and star-shaped compounds.⁹

Systematic investigation of OPPs containing various substituents such as alkyl,¹⁰ alkoxy,¹⁰ amine,^{2c,11} carboxylic ester,¹² cyano,¹³ and nitro^{11a,14} groups has revealed that the chemical and physical properties of substituted OPPs depend on the type of substituents and their bonding positions in the OPPs. The substituents on the OPPs bring about improved solubility in organic solvents, and the reactivity of the substituents enables the conversion of OPPs into functional materials. In the case of substituted

OPPs, only a few studies have been conducted on the synthesis of mono-OH-substituted OPPs **OPP(*n*)-OHs** (*n* denotes the number of benzene rings).¹⁵ Therefore, we conducted a study to synthesize **OPP(*n*)-OHs** and elucidate their chemical properties.

OPP(*n*)-OH will exhibit unique optical properties after the deprotonation of the OH group. This is because the solvation behavior of deprotonated products, i.e., **OPP(*n*)-O[−]**, is quite different from that of **OPP(*n*)-OHs**. In many cases, the solvation of ionic aromatic compounds containing phenoxy groups significantly affects their optical properties. For example, Reichardt's betaine (**1**)¹⁶ and Brooker's merocyanines (**2**)¹⁷ exhibit solvatochromism, which depends on solvent polarity.

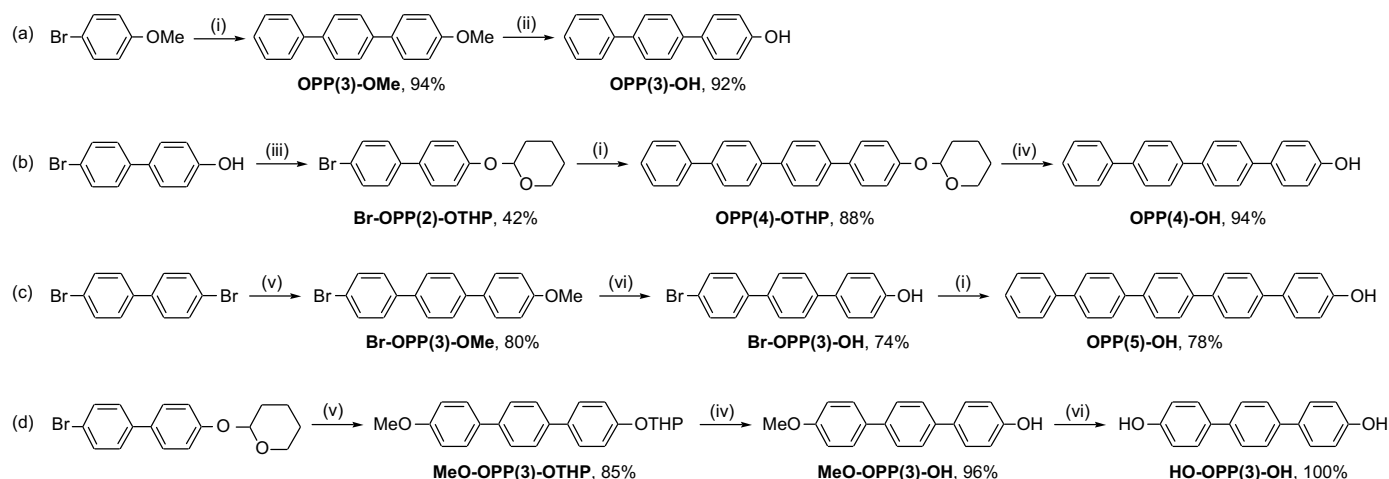


It has been reported that **OPP(2)-OH** and **OPP(3)-OH** cause a bathochromic shift of absorption by the deprotonation.¹⁸ However, the absorption of **OPP(*n*)-OHs** and **OPP(*n*)-O[−]s** (*n*≥4) and fluorescence of **OPP(*n*)-OHs** and **OPP(*n*)-O[−]s** (*n*≥3) have not yet been elucidated. An investigation of the chemical properties of **OPP(*n*)-OHs** (*n*≥3) and their deprotonated products would help us to gain a better understanding of the optical properties of OPPs and develop new functional materials.

OPPs with hydroxyl groups located at both ends, i.e., **HO-OPP(*n*)-OHs**, can be used in the synthesis of functional polymers. For example, poly(aryl ether)s synthesized by polymerization using

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Scheme 1. Synthesis approaches for hydroxyoligo(*p*-phenylene)s **OPP(*n*)-OH** (*n*=3, 4, and 5) and dihydroxy-*p*-terphenyl **HO-OPP(3)-OH**. (i) 4- $\text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{B}(\text{OH})_2$, 1.5 mol % of $\text{Pd}(\text{PPh}_3)_4$, K_2CO_3 (aq), THF, reflux, 48 h; (ii) BBr_3 , CH_2Cl_2 , rt, 30 h; (iii) DHP, CSA, CH_2Cl_2 , rt, 18 h, in dark; (iv) HCl, 1,4-dioxane, 100 °C, 12 h; (v) 4- $\text{MeOC}_6\text{H}_4\text{B}(\text{OH})_2$, 1.5 mol % of $\text{Pd}(\text{PPh}_3)_4$, K_2CO_3 (aq), THF, reflux, 48 h; (vi) $\text{C}_5\text{H}_5\text{N}\cdot\text{HCl}$, 180 °C, 12 h.

HO-OPP(4)-OH exhibit photoluminescence with high quantum yields because they contain *p*-quaterphenyl.¹⁹ However, the synthesis of **HO-OPP(*n*)-OH** (*n*≥3) often requires severe reaction conditions. For example, **HO-OPP(3)-OH** is synthesized by the hydrolysis of terphenyl-4,4'-disulfonic acid at 330 °C.^{19d} The Suzuki coupling reaction is a versatile method for the synthesis of aromatic oligomeric compounds containing functional groups under mild reaction conditions.²⁰ In this study, **OPP(*n*)-OHs** and **HO-OPP(3)-OH** were synthesized by the Suzuki coupling reaction of *O*-alkylated 4-bromophenol derivatives with aromatic boronic acid and the hydrolysis of the *O*-alkyl group. It has been reported that the substituents on the phenoxy ring of **2** considerably affect its optical properties.^{17d} Therefore, in order to elucidate the effect of the substituents on the phenoxy ring of **OPP(*n*)-OH** on the optical properties, a branched oligophenylene 1,3,5-tri(4-biphenyl)phenol **TBP-OH** was synthesized by the Suzuki coupling reaction using 1,3,5-tribromobenzene as a starting material.

In this study, we report the synthesis of linear oligo(*p*-phenylene)s **OPP(*n*)-OHs** (*n*=3, 4, and 5) and **HO-OPP(3)-OH** containing OH group(s) and a branched oligophenylene **TBP-OH** and describe their solvatochromic behaviors. We also compare the chemical properties of **OPP(*n*)-OHs** with those of **TBP-OH**.

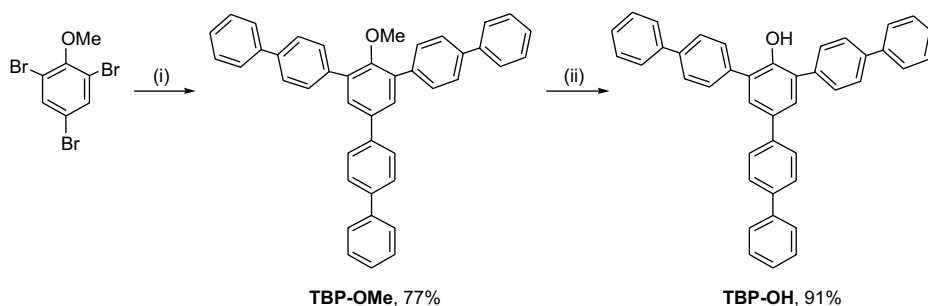
2. Results and discussion

2.1. Synthesis

The oligophenylenes were synthesized by the Suzuki coupling reaction using *O*-alkylated phenol derivatives as substrates and the hydrolysis of the *O*-alkyl group of the coupling products. It is known

that the Suzuki coupling reaction can be carried out on substrates containing the OH group.²⁰ In this study, *O*-alkylated phenols were used as substrates because *O*-alkylated compounds have higher solubility than naked phenols, and therefore, they can be purified easily. Methods for synthesizing hydroxyoligo(*p*-oligophenylene)s **OPP(*n*)-OHs** (*n*=3, 4, and 5) and dihydroxy-*p*-terphenyl **HO-OPP(3)-OH** are shown in Scheme 1.

The reaction of 4-biphenylboronic acid with 4-bromoanisole and 4-bromo-4'-tetrahydropyranyloxybiphenyl **Br-OPP(2)-OTHP** (THP=tetrahydropyranyl) afforded *O*-alkylated oligo(*p*-phenylene)s **OPP(3)-OMe** and **OPP(4)-OTHP** in 94% and 88% yields, respectively. The THP-group-protected compound **Br-OPP(2)-OTHP** was synthesized by the reaction between 4-bromobiphenyl-4'-ol and 3,4-dihydro-2*H*-pyran (DHP). The deprotection of the *O*-methyl and *O*-THP groups of **OPP(3)-OMe** and **OPP(4)-OTHP** yielded the corresponding **OPP(*n*)-OHs** (*n*=3 and 4) in 92% and 94% yields, respectively. The method involving the Suzuki coupling reaction followed by hydrolysis was not used for the synthesis of **OPP(5)-OH**. This is because the solubility of **OPP(5)-OMe** in organic solvents was low, and therefore, it could not be deprotected to produce **OPP(5)-OH**. Instead of the above method, the reaction between 4-bromo-4''-hydroxy[1,1':4',1'']terphenyl **Br-OPP(3)-OH** and 4-biphenylboronic acid was used for the synthesis of **OPP(5)-OH**. The yield of **OPP(5)-OH** (78%) was low apparently because of the use of the unprotected substrate **Br-OPP(3)-OH**. The intermediate compound **Br-OPP(3)-OH** was synthesized by the 1:1 Suzuki coupling reaction of 4,4'-bromobiphenyl with 4-methoxyphenylboronic acid and the hydrolysis of the *O*-methyl group. The use of an excess amount of 4,4'-bromobiphenyl prevented the 2:1 side reaction with 4-methoxyphenylboronic acid and yielded an



Scheme 2. Synthesis of 1,3,5-tri(4-biphenyl)phenol. (i) 4- $\text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{B}(\text{OH})_2$, 1.5 mol % of $\text{Pd}(\text{PPh}_3)_4$, K_2CO_3 (aq), THF, reflux, 48 h; (ii) BBr_3 , CH_2Cl_2 , rt, 30 h.

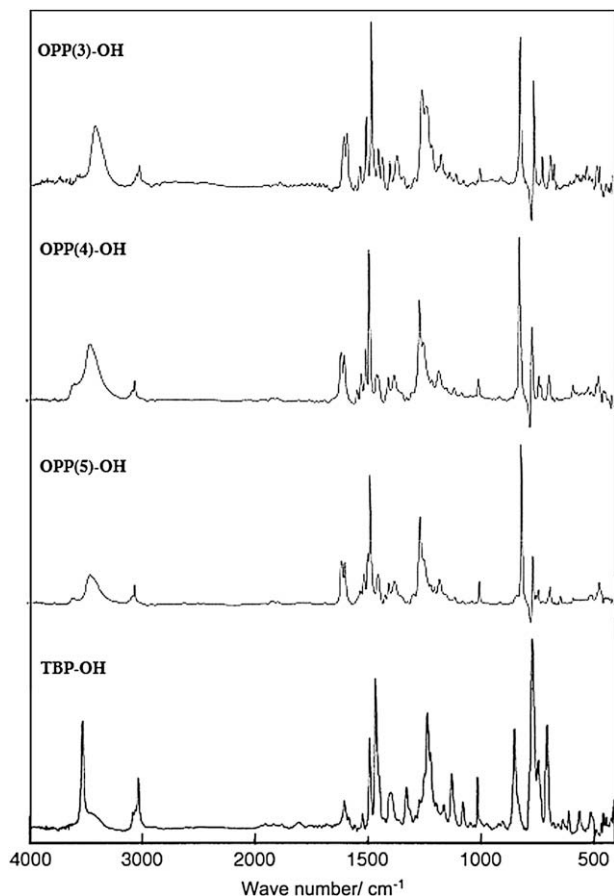


Figure 1. IR spectra of **OPP(n)-OH** ($n=3, 4$, and 5) and **TBP-OH**.

expected product as a precipitate from the reaction mixture. Dihydroxy-*p*-terphenyl **HO-OPP(3)-OH** was obtained via the two-step deprotection of **MeO-OPP(3)-OTHP**, as shown in Scheme 1d. **MeO-OPP(3)-OH** could not be deprotected by using BBr_3 because of the low solubility of the substrate in CH_2Cl_2 ; hence, it was deprotected by using pyridinium hydrochloride.

As shown in Scheme 2, **TBP-OH** was obtained by the 1:3 Suzuki coupling reaction of 1,3,5-tribromoanisole with 4-biphenylboronic acid and the hydrolysis of the methyl group.

The structures of the newly synthesized compounds **OPP(n)-OHs**, **HO-OPP(3)-OH**, and **TBP-OH** were determined by ^1H and ^{13}C NMR spectroscopy and elemental analysis. *p*-Terphenyl and *p*-quaterphenyl were highly soluble in non-polar organic solvents such as cyclohexane and toluene. In contrast, **OPP(n)-OHs** ($n=3$ and 4) and **HO-OPP(3)-OH** were sparingly soluble in non-polar organic

solvents but completely soluble in polar organic solvents such as 1,4-dioxane, *N,N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) because they contained OH group(s). Although the solubility of **OPP(5)-OH** in polar organic solvents was low, it was possible to perform UV-vis and photoluminescence measurements on it.

The melting points of **OPP(n)-OHs** ($n=3$ and 4) determined by DSC measurements were 277°C and 358°C , respectively; these values were higher than those of **OPP(n)s** reported earlier (212°C , $n=3$ and 312°C , $n=4$),²¹ apparently due to intermolecular hydrogen bonding. The melting points of **OPP(n)-ORs** (233°C , $n=3$; $\text{R}=\text{Me}$ and 221°C , $n=4$; $\text{R}=\text{THP}$) were lower than those of **OPP(n)-OHs** ($n=3$ and 4); this result supports the above-mentioned assumption. The melting points of **TBP-OH** and **TBP-OMe** were 216°C and 113°C , respectively.

2.2. IR spectra

Figure 1 shows IR spectra of **OPP(n)-OHs** ($n=3, 4$, and 5) and **TBP-OH**. The main features of the IR spectra of **OPP(n)-OHs** are identical: the absorption peak at 3428 cm^{-1} is due to O–H stretching vibrations; the strong peak at 1484 cm^{-1} is due to phenyl ring vibrations; and the bands at approximately 820 cm^{-1} and 760 cm^{-1} are due to the out-of-plane C–H bending of *p*-phenylene and terminal phenyl rings, respectively. These absorption band positions are similar to those of poly(*p*-phenylene).²² The intensities of absorptions due to the out-of-plane C–H bending of the *p*-phenylene and terminal phenyl rings were used to estimate the degree of polymerization of poly(*p*-phenylene).²² The absorption ratios I_{820}/I_{760} of **OPP(n)-OHs** ($n=3, 4$, and 5) were 1.4, 2.3, and 3.2, respectively; they were largely consistent with the number of *p*-phenylene rings in these compounds.

In contrast to the broad absorption due to the hydrogen bonding OH group of **OPP(n)-OHs**, the absorption due to the O–H stretching vibration of **TBP-OH** is observed as a sharp peak at 3524 cm^{-1} . This observation is attributed to the inhibition of intermolecular hydrogen bonding caused by the bulky biphenyl groups at the 2,6-positions of **TBP-OH**.

2.3. ^1H NMR data

The ^1H NMR chemical shifts of **OPP(n)-OHs** ($n=3, 4$, and 5) and their deprotonated species are summarized in Table 1. Deprotonation of the OH group(s) of **OPP(n)-OHs** and **HO-OPP(3)-OH** was carried out by treating them with an excess amount of NaH in $\text{DMSO}-d_6$. The disappearance of the OH signal in the ^1H NMR spectra of solutions of **OPP(n)-OHs** and NaH indicated that sodium phenoxidation proceeded quantitatively. The signals due to particular protons of **OPP(n)-ONa** shifted to higher magnetic fields as compared to those of **OPP(n)-OH**. The changes in the chemical shift

Table 1

^1H NMR chemical shifts of **OPP(n)-OH** and **HO-OPP(3)-OH** as well as their deprotonated products in $\text{DMSO}-d_6$

	Chemical shift (ppm)												
	H2	H3	H2'	H3'	H2''	H3''	H4''	H2'''	H3'''	H4'''	H2''''	H3''''	H4''''
OPP(3)-OH	6.85	7.54	^a	^a	^a	7.47	7.34	—	—	—	—	—	—
OPP(3)-ONa	6.22	7.18	7.51	7.56	7.64	7.42	7.29	—	—	—	—	—	—
OPP(4)-OH	6.86	7.55	7.69	7.73	7.77	7.79	—	7.81	7.48	7.38	—	—	—
OPP(4)-ONa	6.17	7.18	7.52	7.62	7.71	7.73	—	7.75	7.47	7.37	—	—	—
OPP(5)-OH	6.87	7.56	7.70	7.73	^b	^b	—	^b	^b	—	^b	7.49	7.38
OPP(5)-ONa	6.20	7.19	7.53	7.64	7.73	7.74	—	—	—	—	7.83	7.48	7.37
HO-OPP(3)-OH	6.84	7.51	7.60	7.60	7.51	6.84	—	—	—	—	—	—	—
NaO-OPP(3)-ONa	6.68	7.38	7.52	7.52	7.38	6.68	—	—	—	—	—	—	—

^a Observed in the range of δ 7.65–7.71.

^b Observed in the range of δ 7.78–7.83.

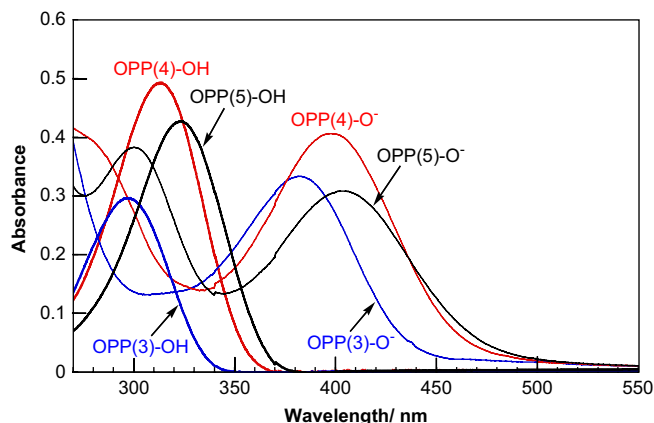


Figure 2. UV-vis spectra of **OPP(n)-OH** ($n=3, 4$, and 5) (bold curves) and their deprotonated species (thin curves) in DMSO (1.0×10^{-5} M).

$\Delta\delta$ increase when the distance of the protons from the ONa group decreases; that is, $\Delta\delta$ is the largest in the case of protons (H^3) adjacent to the ONa group. These observations can be attributed to the electron-donating effect of the ONa group. In contrast, chemical shifts due to the protons of the terminal phenyl ring are almost constant after the deprotonation. These data indicated the possibility of the occurrence of a shift of charge from the phenolate group to the adjacent rings in the deprotonated species. Such a charge shift in **OPP(n)-ONa** may significantly affect its optical properties. In the case of **HO-OPP(3)-OH**, 1H NMR peak shifts due to deprotonation were observed. However, $\Delta\delta$ of **HO-OPP(3)-OH** after deprotonation was smaller than $\Delta\delta$'s of **OPP(n)-OHs**. This is apparently because a charge accepting site is limited in the central phenylene ring.

2.4. UV-vis absorption and solvatochromism

Figure 2 shows the UV-vis spectra of **OPP(n)-OHs** ($n=3, 4$, and 5) in DMSO. The optical data are summarized in Table 2. The absorption maxima ($\lambda_{\max}$ s) of **OPP(n)-OHs** shifted progressively toward longer wavelengths due to the expansion of the π -conjugation system as the number of benzene rings increased. The $\lambda_{\max}$ values were somewhat higher than those of **OPP(n)s** ($n=3, 4$, and 5) reported earlier, which is comparable to the fact that **OPP(n)s** having an electron-donating alkyl group at the 4-position exhibit $\lambda_{\max}$ at a longer wavelength than that of the intact **OPP(n)s**.^{10b}

The treatment of the DMSO solutions of **OPP(n)-OHs** ($n=3, 4$, and 5) and **HO-OPP(3)-OH** with NaH causes bathochromic shift of $\lambda_{\max}$ by approximately 80 nm. The formation of **OPP(n)-ONa** and **NaO-OPP(n)-ONa** was mainly responsible for the shift of $\lambda_{\max}$ toward a longer wavelength. It has been reported that $\lambda_{\max}$ of

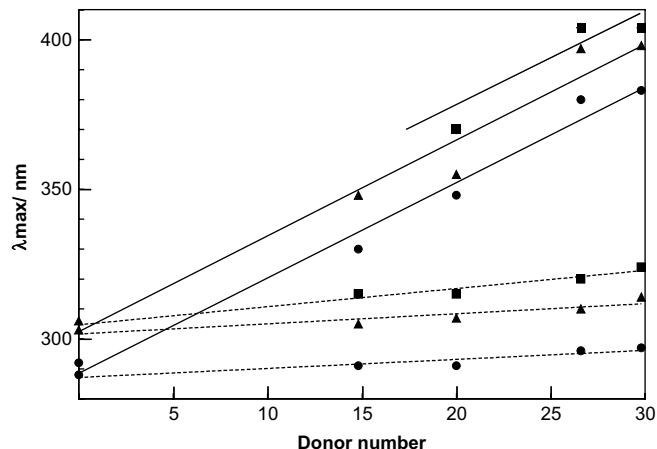


Figure 3. Dependence of $\lambda_{\max}$ of **OPP(n)-OH** ($n=3$ (●), 4 (▲), and 5 (■); dotted line) and their deprotonated species (solid line) on the DN of solvents.

4-hydroxybiphenyl in a phosphate buffer (pH=6.76) shifts to a longer wavelength by 29 nm due to deprotonation.¹⁸ To prove that these observations were due to the deprotonation of the OH group after treatment with NaH, we confirmed that there was no change in the absorption spectra of **OPP(3)-OMe** and **OPP(4)-OTHP** after the addition of NaH. The possibility that aggregation contributes to the solvatochromic behavior through the formation of dimers or other more complex structures can be discarded because the solutions always obey the Lambert–Beer law over several orders of concentration. In order to observe the bathochromic shift of $\lambda_{\max}$, the deprotonation of **OPP(n)-OHs** was carried out by using LiOH and KOH instead of NaH. The degree of bathochromic shift was independent of the type of alkaline metal.

Bathochromic shift attributable to deprotonation depends on the donor number (DN) of the solvents. As shown in Figure 3, the $\lambda_{\max}$ values of **OPP(3)-OH** and **OPP(3)-ONa** shifted to longer wavelengths as the DN of the solvents increased. In contrast to the small bathochromic shift of **OPP(3)-OH** with an increase in the DN of the solvents, the $\lambda_{\max}$ values of the deprotonated species move from 292 nm in CH_2Cl_2 (DN=0) to 398 nm in DMSO (DN=29.8) through to a value of 355 nm in THF (DN=20.0). The large $\Delta\lambda$ value can be attributed to the fact that solvents with a high DN solvate effectively with Na^+ to stabilize the deprotonated species in the solutions. Similar solvatochromic behavior was observed in the case of **OPP(n)-OHs** ($n=4$ and 5) and **OPP(n)-ONas** ($n=4$ and 5), as shown in Figure 3. In relation to the linear relationship shown in Figure 3, the absorption positions of **OPP(n)-OHs** ($n=3$ and 4) and **OPP(n)-ONas** ($n=3$ and 4) in methanol deviated from the plot. This is consistent with the fact that solutions of the phenolate ion in hydrogen bonding solvents cause hypsochromic shift.^{18a}

Table 2
Absorption of **OPP(n)-OH**, **HO-OPP(3)-OH**, and **TBP-OH** as well as their deprotonated products^a

Solvent	DN ^b	OPP(n)-OH (nm)			OPP(n)-ONa (nm)			HO-OPP(3)-OH (nm)	NaO-OPP(3)-ONa (nm)	OBP-OH (nm)	OBP-ONa (nm)
		$n=3$	$n=4$	$n=5$	$n=3$	$n=4$	$n=5$				
Dichloromethane	0	288	303	^c	292	306	^c	292	306	^c	^c
1,4-Dioxane	14.8	291	305	316	330	348	298	294	327	276	264, 356
Methanol	19.0	289	303	^c	313	324	^c	293	321	281	269, 341
THF	20.0	291	307	315	348	355	357	295	341	283	266, 369
DMF	29.6	296	310	321	380	397	404	299	376	283	400
DMSO	29.8	297	314	324	383	398	404	302	377	284	402

^a Concentration of solution was 1.0×10^{-5} M.

^b DN=donor number.

^c Not measured due to low solubility.

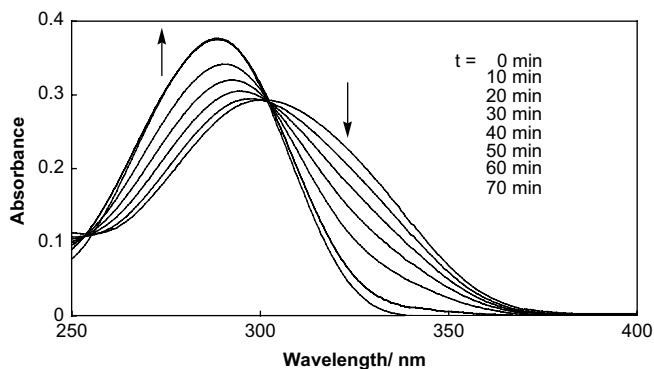


Figure 4. Changes of UV-vis spectra of methanol solution of **OPP(3)-OH** (1×10^{-5} M) in the presence of aqueous solution of NaOH (0.5×10^{-5} M) with time upon standing under nitrogen at 30 °C.

The bathochromic shift of **OPP(n)-OHs** caused by deprotonation was significantly affected by the concentration of the base. The absorption of the methanol solutions of **OPP(3)-OH** in the presence of NaOH (aq), which was less than the equimolar amount of **OPP(3)-OH**, varied with the time for which they were left to stand under nitrogen; that is, the absorption due to **OPP(3)-ONa** decreased and that due to **OPP(3)-OH** increased simultaneously, as shown in Figure 4. In contrast, the UV-vis spectra of the methanol solutions of **OPP(3)-OH** in the presence of an excess amount of the base remained almost unchanged over time. **OPP(n)-OHs** ($n=4$ and 5) showed similar absorption behavior. These results suggested that intact **OPP(n)-OHs** and their deprotonated species in solution were in equilibrium.

Bathochromic shift caused by deprotonation was observed in the case of **HO-OPP(3)-OH**. However, it was smaller than that of **OPP(n)-ONas** ($n=3, 4$, and 5). In the case of **OPP(n)-ONas**, the intramolecular charge shift from the phenoxy groups to the adjacent rings appeared to contribute to the bathochromic shift. It may be assumed that the smaller bathochromic shift of **NaO-OPP(3)-ONa** was caused by a slight shift of charge from the phenolate groups at both ends to the central phenylene ring. This assumption is in good agreement with the result that the ^1H NMR peak shifts of **HO-OPP(3)-OH** produced by deprotonation are smaller than those of **OPP(n)-OHs**.

The solutions of **TBP-OH** exhibited λ_{max} at approximately 280 nm, irrespective of the type of solvent. The wavelength at which λ_{max} was observed was shorter than that of **OPP(3)-OH**, although **TBP-OH** consisted of seven benzene rings. A possible reason for these observations is that the degree of twisting between the three biphenyl substituents and the central phenylene unit is larger than that between the adjacent benzene rings in **OPP(n)-OHs**. It has been reported that the three phenyl substituents on the central

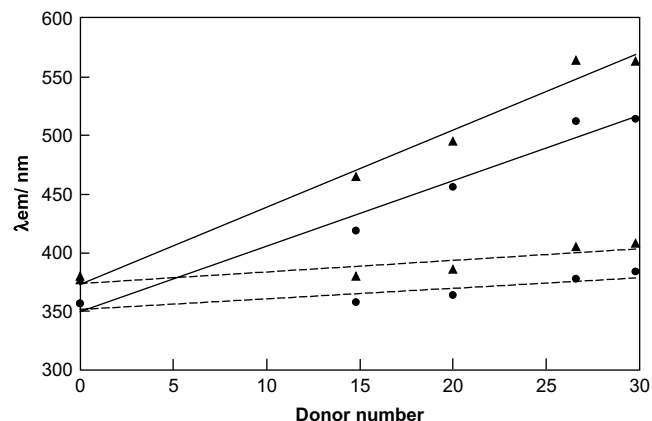


Figure 5. Dependence of PL peak position of **OPP(n)-OH** ($n=3$ (●) and 4 (▲); dotted line) and their deprotonated species (solid line) on the DNs of solvents.

phenylene unit in π -conjugated compounds with a 1,3,5-triphenylbenzene core are twisted by approximately 45°. The twisting between the adjacent phenylene rings of **OPP(n)** ($3 \leq n \leq 8$) is estimated to be approximately 10–37°. As in the case of **OPP(n)-ONas**, λ_{max} of the deprotonated species of **TBP-OH** shifted to a longer wavelength as the DNs of the solvents increased.

2.5. Photoluminescence

It has been reported that OPPs exhibit photoluminescence (PL) with a high quantum yield.^{10b,24} Hydroxyoligo(*p*-phenylene)s **OPP(n)-OHs** ($n=3, 4$, and 5) and their deprotonated species **OPP(n)-ONas** ($n=3, 4$, and 5) are photoluminescent in solution. The PL data are summarized in Table 3. The PL peak positions of **OPP(n)-OHs** ($n=3, 4$, and 5) were observed at longer wavelengths than those of **OPP(n)s** ($n=3, 4$, and 5) in solution.^{10b,24} These observations are comparable to the fact that OPPs having an electron-donating alkoxy group **OPP(n)-OR** exhibit PL peaks at longer wavelengths than **OPP(n)**.^{10b} The quantum yields of the PLs of the 1,4-dioxane solutions of **OPP(n)-OHs** ($n=3, 4$, and 5) were 59, 42, and 59%, respectively; these values were lower than those of **OPP(n)s** ($n=3, 4$, and 5) reported earlier.²⁴

The emission peak positions of **OPP(n)-OHs** and **OPP(n)-ONas** depended on the DNs of the solvents; that is, the emission color can be tuned by changing the solvent. For example, **OPP(4)-ONa** exhibited purple, blue, green, and orange emissions after it was irradiated with UV light in CH_2Cl_2 (DN=0), 1,4-dioxane (DN=14.8), THF (DN=20.0), and DMSO (DN=29.8), respectively, as shown in Figure 5. Figure 6 shows the dependence of the emission peak positions of **OPP(n)-OHs** ($n=3$ and 4) on the DNs of the solvents. Thus, by alternating solvents such as CH_2Cl_2 , which have a small DN

Table 3

Photoluminescence data of **OPP(n)-OH**, **HO-OPP(3)-OH**, and **TBP-OH** as well as their deprotonated products^a

Solvent	DN ^b	OPP(n)-OH (nm)			OPP(n)-ONa (nm)			HO-OPP(3)-OH (nm)	NaO-OPP(3)-ONa (nm)	OBP-OH (nm)	OBP-ONa (nm)
		$n=3$	$n=4$	$n=5$	$n=3$	$n=4$	$n=5$				
Dichloromethane	0	357	380	^c	357	377	^c	344, 357	^c	^c	^c
1,4-Dioxane	14.8	358	380	397	419	465	483	346, 359	410	390	504
Methanol	19.0	371	397	^c	475	524	^c	348, 361	411	393	504
THF	20.0	364	386	399	456	495	509	347, 361	407	393	503
DMF	29.6	378	405	409	512	562	^d	351, 366	435	402, 521	527
DMSO	29.8	384	408	414	514	563	^d	355, 370	439	404, 520	529

^a Concentration of solution was 1.0×10^{-5} M.

^b DN=donor number.

^c Not measured due to low solubility.

^d No photoluminescence.

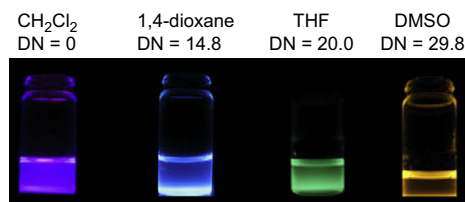


Figure 6. Photographs of **OPP(4)-ONa** when it was irradiated with UV light in CH_2Cl_2 (DN=0), 1,4-dioxane (DN=14.8), THF (DN=20.0), and DMSO (DN=29.8).

value, and those such as DMF and DMSO, which have large DN values, it is observed that the emission peak positions of **OPP(n)-OHs** ($n=3$ and 4) shifts only by approximately 30 nm. However, a significantly large shift in the emission peaks of **OPP(n)-ONas** ($n=3$ and 4) occurred as the DN of the solvents increased. These observations are comparable to the results that λ_{max} of **OPP(n)-ONa** in solution shifts to a longer wavelength than that of **OPP(n)-OH** with an increase in the DN of the solvents. The remarkable solvatochromic shift of the PL peak position of **OPP(n)-ONa** appeared to be due to the charge shift from the phenolate group to the adjacent rings. In addition to the charge shift effect, a large amount of stabilization energy produced by the solvation of **OPP(n)-ONa** may contribute to the solvatochromic red shift as the DN of the solvents increase. In the case of anthrylphenoxide anions, the solvatochromic red shift of the PL peak position occurred as the dielectric constant of the solvents increased.²⁵ In relation to the linear relationship shown in Figure 5, the emission peak positions of **OPP(n)-OHs** ($n=3$ and 4) and **OPP(n)-ONas** ($n=3$ and 4) in methanol deviated from the plot. This appears to be due to the assumption that **OPP(n)-OHs** ($n=3$ and 4) and **OPP(n)-ONas** ($n=3$ and 4) form a hydrogen bond with methanol. It has been reported that hydroxyarenes such as naphthol cause bathochromic shift of the fluorescence peak when they form a hydrogen-bonded complex.²⁶ The PL intensities of **OPP(n)-ONa** decreased as the chain length (n) increased. These phenomena were significant in the case of organic solvents that had high DN values, such as DMF and DMSO. For example, **OPP(5)-ONa** did not exhibit PL in the solvents. Reasons for quenching of the PL of **OPP(5)-ONa** in DMF and DMSO are not entirely clear.

The concentration of the base significantly affected on the emission behavior of the solutions of **OPP(n)-OHs** ($n=3$, 4, and 5). Figure 7 shows the PL spectra of the methanol solutions of **OPP(3)-OH** containing different amounts of NaOH. It is observed that the peak at 371 nm decreases and a new emission peak at 475 nm appears as the concentration of the base increases. This result confirms the fact that the emission peaks at 371 nm and 475 nm

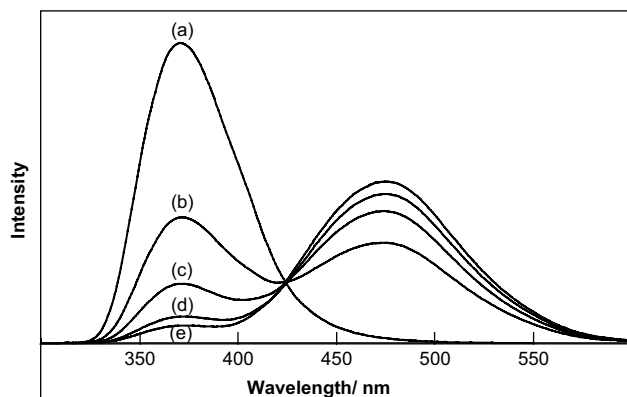


Figure 7. PL spectra of methanol solutions of **OPP(3)-OH** (1×10^{-8} M) in the presence of various amounts of NaOH. (a); 0 M, (b); 0.5×10^{-8} M, (c); 1×10^{-8} M, (d); 2×10^{-8} M, (e); 3×10^{-8} M.

originate from **OPP(3)-OH** and **OPP(3)-ONa**, respectively. The PL spectra of the solutions of **OPP(3)-OH** in the presence of a less equimolar amount of NaOH changed with the time for which the solutions were left to stand under nitrogen; that is, absorption due to **OPP(3)-ONa** at 475 nm decreased and that due to **OPP(3)-OH** at 371 nm increased simultaneously. On the other hand, the PL spectra of the solution of **OPP(3)-OH** in the presence of an excess amount of NaOH did not change over time. These observations are consistent with the UV-vis absorption behavior that depends on the concentration of the base, as mentioned above.

As mentioned earlier, an increase in the DN of the solvents caused the large bathochromic shift of the PL peaks of **OPP(n)-ONas** ($n=3$, 4, and 5). However, the DN of the solvents had a small effect on the peak positions of **TBP-OH** and **TBP-ONa**. Their PL peaks appeared at approximately 390 nm and 500 nm when they were dissolved in solvents with moderate DN, such as 1,4-dioxane (DN=14.8) and THF (DN=20), respectively. The PL peak position of **TBP-ONa** in 1,4-dioxane was comparable to that of **OPP(4)-ONa** in DMSO (DN=29.8). These observations can be attributed to the steric effect of the biphenyl substituents at the 2,6-positions that can stabilize the phenolate anion in the S^1 -excited state even in solvents with moderate DN values. It was reported that **OPP(n)** adopted more planar configurations in the S^1 -excited than in the S^0 -ground state.²⁵ Hence, in the S^1 -excited state, the three biphenyl substituents of **TBP-OH** could adopt a more planar configuration with the phenylene core. Because of this configuration, the wavelength at which the PL peak of **TBP-OH** appeared at longer than the wavelengths at which the PL peaks of **OPP(n)-OHs** appeared; however, the solutions of **TBP-OH** showed λ_{max} at shorter wavelengths than those of **OPP(n)-OHs**. The quantum yields of the PLs of the 1,4-dioxane solutions of **TBP-OMe** and **TBP-OH** are 15 and 21%, respectively.

3. Conclusions

Oligophenylenes containing hydroxyl group(s), namely, **OPP(n)-OHs**, **HO-OPP(3)-OH**, and **TBP-OH**, were synthesized by the Suzuki coupling reaction. The OH group contributed to improve the solubility and melting points of **OPP(n)-OHs**. The treatment of **OPP(n)-OHs** with a base produced deprotonated species **OPP(n)-ONas**, whose absorption and PL peak positions in solution shifted toward longer wavelengths with an increase in the DN of the solvents. The emission colors of the solutions of **OPP(n)-ONas** could be tuned by changing the solvent. The optical properties of the oligophenylenes containing OH group(s) were significantly affected by the arrangement of their phenylene rings. From the results of this study, it can be concluded that new luminescent materials can be developed on the basis of the remarkable solvatochromic behavior of **OPP(n)-ONas**.

4. Experimental section

4.1. General

Solvents were dried, distilled, and stored under nitrogen. 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 a JEOL AL-400 spectrometer, respectively. Elemental analysis was performed on a Yanagimoto MT-5 CHN coder. UV-vis and PL spectra were obtained by 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.

4.2. Synthesis of OPP(3)-OMe

4-Bromoanisole (1.14 g, 6.1 mmol) and 4-biphenylboronic acid (1.10 g, 5.5 mmol) were dissolved in 40 mL of dry THF under N₂. To the solution were added K₂CO₃ (aq) (2.0 M, 20 mL; N₂ bubbled before use), Pd(PPh₃)₄ (0.10 g, 0.90 mmol), and several drops of the phase transfer catalyst (Aliquat 336). After the mixture was refluxed for 48 h, the solvent was removed under vacuum. The resulting solid was washed with water and dried under vacuum to give a light yellow solid, which was purified by silica gel column chromatography (eluent=CHCl₃). The solvent was removed by evaporation and a resulting solid was dried in vacuo to give **OPP(3)-OMe** as a white powder (1.36 g, 94%). ¹H NMR (400 MHz, CDCl₃): δ 7.63–7.67 (m, 6H), 7.58 (d, *J*=8.8 Hz, 2H), 7.46 (t, *J*=7.6 Hz, 2H), 7.33 (t, *J*=7.6 Hz, 1H), 7.00 (d, *J*=8.8 Hz, 2H), 3.87 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 159.2, 140.8, 139.7, 139.5, 133.2, 128.8, 128.0, 127.4, 127.2, 127.0, 114.2, 55.4. Mp=233 °C.

4.3. Synthesis of OPP(3)-OH

A dichloromethane solution (10 mL) of BBr₃ (0.80 mL, 8.4 mmol) was added dropwise to a dichloromethane solution (50 mL) of **OPP(3)-OMe** (0.50 g, 1.9 mmol). The solution was stirred at 25 °C for 30 h. After the solution was washed with water, the solvent was removed under vacuum. The resulting solid was washed with water and then chloroform (30 mL). **OPP(3)-OH** was collected by filtration, dried under vacuum, and obtained as a white powder (0.34 g, 92%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.57 (s, 1H), 7.65–7.71 (m, 6H), 7.54 (d, *J*=8.8 Hz, 2H), 7.47 (t, *J*=7.2 Hz, 2H), 7.34 (t, *J*=7.2 Hz, 1H), 6.85 (d, *J*=8.4 Hz, 2H). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ 157.2, 139.7, 139.2, 138.0, 130.3, 128.9, 127.6, 127.3, 127.0, 126.4, 126.3, 115.7. Anal. Calcd for C₁₈H₁₄O: C, 87.78; H, 5.73. Found: C, 87.70; H, 5.77. Mp=277 °C.

4.4. Synthesis of Br-OPP(2)-OTHP

To a dichloromethane suspension (60 mL) of 4-bromo-4'-hydroxybiphenyl (3.00 g, 12.1 mmol) was added 3,4-dihydro-2H-pyran (3.26 mL, 38.4 mmol) and camphor-10-sulfonic acid (0.082 g, 0.35 mmol). After the suspension was stirred at 25 °C for 18 h in the dark, the solvent was removed under vacuum. The resulting solid was extracted with ether and dried over magnesium sulfate. The solvent was removed under vacuum and the resulting solid was washed with hexane. **Br-OPP(2)-OTHP** was collected by filtration, dried under vacuum, and obtained as a white powder (1.66 g, 42%). ¹H NMR (400 MHz, CDCl₃): δ 7.53 (d, *J*=8.8 Hz, 2H), 7.47 (t, *J*=8.4 Hz, 2H), 7.41 (t, *J*=8.8 Hz, 2H), 7.12 (d, *J*=8.8 Hz, 2H), 5.47 (t, *J*=2.8 Hz, 1H), 3.92 (m, 1H), 3.64 (m, 1H), 2.03 (m, 1H), 1.89 (m, 2H), 1.55–1.69 (m, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 156.8, 139.8, 133.3, 131.8, 128.3, 127.9, 120.8, 116.8, 96.3, 62.0, 30.3, 25.2, 18.7.

4.5. Synthesis of OPP(4)-OTHP

OPP(4)-OTHP was synthesized by the Suzuki coupling reaction of **Br-OPP(2)-OTHP** with 4-biphenylboronic acid. Yield=88%. ¹H NMR (400 MHz, CDCl₃): δ 7.66–7.74 (m, 10H), 7.58 (d, *J*=8.8 Hz, 2H), 7.47 (t, *J*=7.6 Hz, 2H), 7.37 (d, *J*=7.6 Hz, 1H), 7.15 (d, *J*=8.8 Hz, 2H), 5.49 (t, *J*=2.8 Hz, 1H), 3.96 (m, 1H), 3.65 (m, 1H), 2.04 (m, 1H), 1.90 (m, 2H), 1.55–1.71 (m, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 156.7, 140.7, 140.1, 139.9, 139.7, 139.0, 138.8, 134.0, 128.8, 128.0, 127.5, 127.3, 127.1, 127.0, 116.8, 96.4, 62.1, 30.9, 30.4, 25.2, 18.8. Mp=221 °C.

4.6. Synthesis of OPP(4)-OH

To a 1,4-dioxane and methanol (v/v=8:1) solution (90 mL) of **OPP(4)-OTHP** was added hydrochloric acid (20 mL). After the

solution was stirred at 100 °C for 12 h, the solution was neutralized with NaOH (aq). The solvents were removed under vacuum and the resulting solid was washed with water. **OPP(4)-OH** was collected by filtration, dried under vacuum, and obtained as a white powder (0.16 g, 94%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.57 (s, 1H), 7.68–7.82 (m, 10H), 7.55 (d, *J*=8.8 Hz, 2H), 7.48 (t, *J*=7.6 Hz, 2H), 7.38 (t, *J*=7.6 Hz, 1H), 6.86 (d, *J*=8.8 Hz, 2H). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ 157.0, 139.4, 139.1, 138.2, 138.5, 137.2, 130.1, 128.6, 127.3, 127.2, 126.9, 126.6, 126.2, 126.1, 115.6. Anal. Calcd for C₂₄H₁₈O·0.1H₂O: C, 88.91; H, 5.66. Found: C, 88.98; H, 5.70. Mp=358 °C.

4.7. Synthesis of Br-OPP(3)-OMe

Br-OPP(3)-OMe was synthesized by the 1:1 Suzuki coupling reaction of 4,4'-dibromobiphenyl with 4-methoxyphenylboronic acid. ¹H NMR (400 MHz, CDCl₃): δ 7.56–7.62 (m, 8H), 7.55 (d, *J*=8.8 Hz, 2H), 7.00 (t, *J*=8.8 Hz, 2H), 3.87 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 159.3, 140.1, 139.7, 138.2, 133.0, 131.9, 128.6, 128.1, 127.25, 127.16, 121.5, 114.3, 55.4.

4.8. Synthesis of Br-OPP(3)-OH

Br-OPP(3)-OMe was dissolved in melting pyridine hydrochloric acid (20 g) at 180 °C and the solution was stirred at the temperature for 12 h. After the solution was cooled to room temperature, a precipitate from the solution was washed with water and extracted with methanol. The solvent removed under vacuum and the resulting solid was dried in vacuo to give **Br-OPP(3)-OH** as a white solid (0.28 g, 74%). ¹H NMR (400 MHz, CDCl₃): δ 7.49–7.61 (m, 10H), 6.93 (d, *J*=8.8 Hz, 2H), 4.84 (s, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 157.3, 139.6, 138.9, 136.7, 131.8, 130.2, 128.6, 127.7, 127.0, 126.5, 120.8, 115.8.

4.9. Synthesis of OPP(5)-OH

OPP(5)-OH was synthesized by the Suzuki coupling reaction of **Br-OPP(3)-OH** with 4-biphenylboronic acid. Yield=78%. ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.58 (s, 1H), 7.78–7.83 (m, 10H), 7.73 (d, *J*=7.6 Hz, 2H), 7.70 (d, *J*=8.8 Hz, 2H), 7.56 (d, *J*=8.4 Hz, 2H), 7.49 (t, *J*=8.0 Hz, 2H), 7.37 (t, *J*=8.0 Hz, 1H), 6.87 (d, *J*=8.8 Hz, 2H). Anal. Calcd for C₃₀H₂₂O·0.15H₂O: C, 89.81; H, 5.60. Found: C, 89.81; H, 5.68. Mp=419 °C.

4.10. Synthesis of MeO-OPP(3)-OTHP

MeO-OPP(3)-OTHP was synthesized by Suzuki coupling reaction of **Br-OPP(2)-OTHP** with 4-methoxyphenylboronic acid. Yield=85%. ¹H NMR (400 MHz, CDCl₃): δ 7.55–7.61 (m, 8H), 7.14 (d, *J*=8.4 Hz, 2H), 6.99 (t, *J*=8.4 Hz, 2H), 5.48 (t, *J*=3.2 Hz, 1H), 3.86 (s, 3H), 3.65 (m, 1H), 2.03 (m, 1H), 1.89 (m, 2H), 1.55–1.70 (m, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 159.1, 156.6, 139.2, 134.2, 133.3, 128.0, 127.0, 116.8, 114.2, 96.4, 62.1, 55.4, 30.4, 25.2, 18.8.

4.11. Synthesis of HO-OPP(3)-OH

HO-OPP(3)-OH was synthesized by stepwise hydrolysis of the methoxy and THP groups of **MeO-OPP(3)-OTHP**. Yield=96%. ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.53 (s, 2H), 7.60 (s, 4H), 7.51 (d, *J*=8.8 Hz, 4H), 6.84 (d, *J*=8.4 Hz, 4H). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ 157.1, 138.1, 130.5, 127.5, 126.3, 115.7. Anal. Calcd for C₁₈H₁₄O₂·0.2H₂O: C, 81.43; H, 5.31. Found: C, 81.46; H, 5.10. Mp=378 °C.

4.12. Synthesis of TBP-OMe

TBP-OMe was synthesized by the 1:3 Suzuki coupling reaction of 2,4,6-tribromoanisole with 4-biphenylboronic acid. Yield=77%. ^1H NMR (400 MHz, CDCl_3): δ 7.65–7.79 (m, 20H), 7.45–7.50 (m, 6H), 7.25–7.39 (m, 3H), 3.32 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 154.7, 140.8, 140.6, 140.1, 139.3, 137.6, 136.8, 135.7, 129.7, 128.9, 128.8, 127.5, 127.38, 127.35, 127.1, 127.03, 127.00, 60.8. Mp=168 °C.

4.13. Synthesis of TBP-OH

TBP-OH was synthesized by the hydrolysis of **TBP(3)-OMe** by the use of BBr_3 . Yield=91%. ^1H NMR (400 MHz, CDCl_3): δ 7.64–7.77 (m, 20H), 7.40–7.50 (m, 6H), 7.26–7.38 (m, 3H), 5.56 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 149.2, 140.7, 140.6, 139.8, 139.4, 136.4, 133.5, 129.8, 128.9, 128.8, 128.5, 127.7, 127.55, 127.52, 127.3, 127.15, 127.13, 127.1, 127.0. Mp=216 °C.

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