

Tropolone-Terminated Oligomeric Fluorophores with Responsive Properties to External Environment

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Tropolone-terminated oligomeric fluorophores (Tp2OP, Tp2OPV, and Tp2OPE) were prepared by palladium-catalyzed coupling reactions. A phenylene-type Tp2OP showed an emission maximum in the blue fluorescent region and the fluorescence quantum yield was relatively low. Tp2OPV and Tp2OPE, which included vinylene and ethynylene units as connecting groups, respectively, had emission maxima at longer wavelength regions than Tp2OP. The UV spectra of Tp2OP gradually red shifted as the dielectric constant of solvent increased. Tp2OP exhibited positive solvatofluorochromic behavior, which related to an increase of the dipole moment due to the charge-transfer characteristics of the emitting state. The fluorescence quantum yields (QYs) of fluorophores exponentially fell with increasing MeOH content in THF solution. Upon addition of CuCl₂ to Tp2OP until the ratio of [Cu²⁺]/[Tp2OP] reached 1, the UV spectra exhibited a red-shift. The emission maximum wavelength of Tp2OP blue shifted and a remarkable decrease of the PL intensity was observed. Tp2OP showed metal ion-response, especially in PL spectra.

The development of novel luminescent molecules¹ is an essential topic in chemical applications including optoelectronic devices,² biological chemosensors,³ and metal ion analyses.⁴ Environment-sensitive fluorophores are a special class of chromophores showing responsive spectroscopic behaviors, namely shifts of emission maximum wavelength and changes of fluorescence intensity that are dependent upon the physicochemical properties of the surrounding environment. The emission properties of these kinds of organic materials are tunable via chemical modifications of a base structure that has been extensively explored. Among many organic materials, oligomeric fluorophores bearing π -conjugated systems would be better candidates compared to luminescent conjugated polymers, because they have precisely defined molecular length and can be purified to obtain defect-free compounds. The choice of aromatic segments and their connecting groups can provide access to diverse types of functional fluorophores. We have previously reported the synthesis of a series of conjugated polymers possessing seven-membered non-benzenoid aromatic tropenoid derivatives and found interesting optical properties.⁵ Tropolone, 2-hydroxy-2,4,6-cycloheptatrien-1-one, has an equal double-minimum multidimensional potential energy surface allowing its two equivalent tautomers to interconvert and has been extensively studied from experimental and theoretical points of view.⁶ There are a few reports utilizing tropolone as the key element of functional molecules such as liquid crystalline materials⁷ and antibiotic polymers.⁸ However, to the best of our knowledge, conjugated oligomeric fluorophores containing the tropolone moiety have been hitherto unknown. Since tropolone has a relatively large dipole moment (3.71 debye), a completely planar structure, and an amphiphilic character ($pK_a = 6.7$ and $pK_{BH} = -0.86$), the corresponding fluorophore can be expected

to have fascinating optical properties.⁹ On the other hand, the emission properties of fluorophores having a metal ion-chelating group are influenced by the coordinated metal ions (and of course their counter ions). It has been reported that tropolone complexes with transition-metal ions are more stable than those of β -diketones of comparable acidity¹⁰ and tropolones are suitable ligands for lanthanide metal ions with high coordination number.¹¹ Accordingly, conjugated oligomeric fluorophores containing the tropolone structure also belong to a rather attractive family due to the responsive optical properties to metal ions.

In the present paper, we would like to describe the preparation and optical properties of tropolone-terminated oligomeric fluorophore in the first section and the optical response to metal ions in the second section.

Experimental

General. All reactions were performed under nitrogen unless otherwise noted. Dry diethyl ether (ether) and tetrahydrofuran (THF) were purchased from Aldrich and Kanto Chemical Co., respectively. Dichloromethane (CH₂Cl₂), toluene, hexane, and *N*-methyl-2-pyrrolidone (NMP) were dried over CaH₂ and distilled under nitrogen prior to use. Tetrakis(triphenylphosphine)palladium(0) was purchased from Tokyo Chemical Industry (TCI) Co. Palladium(II) acetate was purchased from Wako Pure Chemical Industry Co. Dichlorobis(triphenylphosphine)palladium(II) was purchased from Aldrich Chemical Co. Other reagents were used as received. Silica gel 60N obtained from Kanto Chemical Co. was used for column chromatography.

Instrumentation. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 200 FT-NMR spectrometer using tetramethylsilane (¹H NMR, δ 0.00) and CDCl₃ (¹³C NMR, δ 77.0) as internal reference peaks. Infrared (IR) spectra were recorded on a Jasco FT-IR 460Plus spectrophotometer

in ATR method. Melting points (Mp) were determined on a Yanagimoto micro melting point apparatus MP-J3. Elemental analyses (EA) were performed on a Perkin-Elmer PE2400II in CHN mode. Ultraviolet (UV) and photoluminescence (PL) spectra were recorded on a Shimadzu UV-1650PC spectrophotometer and a Shimadzu RF-5300PC spectrofluorometer, respectively, using a 1-cm quartz cell. Quantum yields in solution were determined relative to quinine sulfate in 0.05 M H₂SO₄ with a quantum yield of 0.55.

Synthesis of Tropolone-Containing Fluorophores. 1,4-Didecyloxy-2,5-bis(4-hydroxy-5-oxocyclohepta-1,3,6-trienyl)benzene (Tp2OP): To a THF (1.7 mL) solution of 5-bromotropolone (0.05 g, 0.25 mmol) and 2,5-didecyloxy-1,4-phenylenediboronic acid¹² (0.05 g, 0.11 mmol) were added an aqueous solution (0.4 mL) of K₂CO₃ (0.06 g, 0.45 mmol) and Pd(PPh₃)₄ (0.01 g, 0.01 mmol). The mixture was heated to reflux for 2 days and extracted with CHCl₃. The organic phase was washed with diluted aq. HCl, distilled H₂O, and brine. After drying over MgSO₄, precipitation into cold hexane gave 0.06 g yellowish-green solid (79% yield). Mp 127–129 °C. ¹H NMR (200 MHz, CDCl₃): δ 7.57 (d, *J* = 12 Hz, 4H), 7.37 (d, *J* = 12 Hz, 4H), 6.87 (s, 2H), 3.91 (t, *J* = 6.3 Hz, 4H), 1.66 (m, 4H), 1.42–1.01 (br, 28H), 0.86 (t, *J* = 3.4 Hz, 6H). ¹³C NMR (50 MHz, CDCl₃): δ 170.9, 149.8, 139.5, 139.2, 123.3, 115.4, 69.8, 31.8, 29.5, 29.5, 29.3, 29.2, 26.1, 22.6, 14.1. IR (ATR) (cm⁻¹) 3136, 2915, 2850, 1619, 1549, 1509, 1458, 1399, 1360, 1293, 1262, 1214, 1037, 848, 817, 678. Found: C, 74.39; H, 8.73%. Calcd for C₄₀H₅₄O₆·H₂O: C, 74.04; H, 8.70%.

1,4-Didecyloxy-2,5-bis[(E)-(4-hydroxy-5-oxocyclohepta-1,3,6-trienyl)ethenyl]benzene (Tp2OPV): To a NMP (5 mL) solution of 5-bromotropolone (0.05 g, 0.25 mmol), 1,4-didecyloxy-2,5-diethynylbenzene¹³ (0.05 g, 0.11 mmol), and NaOAc (0.03 g, 0.34 mmol) was added Pd(OAc)₂ (2.5 mg, 0.01 mmol). The mixture was heated at 100 °C for 2 days and poured into a large amount of H₂O. CHCl₃ was added and the separated organic phase was washed with diluted aq. HCl, distilled H₂O, and brine. After drying over MgSO₄, the crude product was dissolved again in THF and purified by precipitating into cold hexane to give 0.03 g red solid in 39% yield. Mp 129–130 °C. ¹H NMR (200 MHz, CDCl₃): δ 7.58 (d, *J* = 10 Hz, 4H), 7.44–7.31 (br, 6H), 7.11 (d, *J* = 16 Hz, 2H), 7.07 (s, 2H), 4.06 (t, *J* = 6.3 Hz, 4H), 1.87 (m, 4H), 1.65–0.98 (br, 28H), 0.88 (t, *J* = 6.0 Hz, 6H). IR (KBr) (cm⁻¹) 3221, 2922, 2852, 1611, 1555, 1495, 1455, 1418, 1332, 1261, 1202, 1024, 952, 859, 744. Found: C, 75.09; H, 8.68%. Calcd for C₄₄H₅₈O₆·H₂O: C, 75.39; H, 8.63%.

1,4-Didecyloxy-2,5-bis[(4-hydroxy-5-oxocyclohepta-1,3,6-trienyl)ethynyl]benzene (Tp2OPE): To a solution of 5-bromotropolone (0.05 g, 0.25 mmol) and 1,4-didecyloxy-2,5-diethynylbenzene¹⁴ (0.05 g, 0.11 mmol) in toluene/NEt₃ (2.5 mL/1 mL) were added CuI (2.2 mg, 0.01 mmol) and PdCl₂(PPh₃)₂ (7.9 mg, 1.1 μ mol). The mixture was heated at 70 °C for 2 days and poured into a large amount of H₂O. CHCl₃ was added and the separated organic phase was washed with diluted aq. HCl, distilled H₂O, and brine. After drying over MgSO₄, the crude product was dissolved again in THF and purified by precipitating into cold Et₂O to give 0.04 g of an orange solid in 54% yield. Mp 124–125 °C. ¹H NMR (200 MHz, CDCl₃): δ 7.60 (d, *J* = 12 Hz, 4H), 7.29 (d, *J* = 12 Hz, 4H), 6.97 (s, 2H), 4.03 (t, *J* = 6.2 Hz, 4H), 1.82 (m, 4H), 1.63–0.97 (br, 28H), 0.88 (br, 6H). IR (ATR) (cm⁻¹) 3207, 2923, 2852, 1614, 1556, 1420, 1260, 1207, 1018, 720. Found: C, 75.35; H, 8.08%. Calcd for C₄₄H₅₄O₆·H₂O: C, 75.83; H, 8.10%.

5-Phenyltropolone (Tp1OP): To a THF (3 mL) solution of 5-bromotropolone (0.07 g, 0.33 mmol) and phenylboronic acid

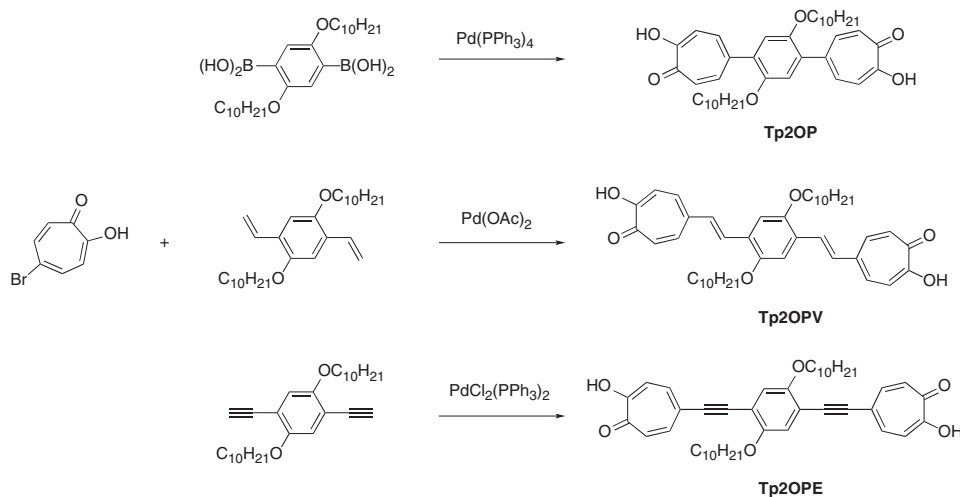
(0.04 g, 0.33 mmol) were added an aqueous solution (0.6 mL) of K₂CO₃ (0.09 g, 0.66 mmol) and Pd(PPh₃)₄ (0.02 g, 0.02 mmol). The mixture was heated to reflux for 2 days and extracted with CH₂Cl₂. The organic phase was washed with diluted aq. HCl, distilled H₂O, and brine. After drying over MgSO₄, purification by SiO₂ chromatography (CHCl₃/MeOH = 19/1 in volume, *R_f* = 0.4) gave 0.05 g of green solid (79% yield). ¹H NMR (200 MHz, CDCl₃): δ 7.63 (d, *J* = 12 Hz, 2H), 7.48–7.36 (br, 7H). ¹³C NMR (50 MHz, CDCl₃): δ 170.8, 142.4, 142.4, 137.7, 132.2, 132.0, 129.0, 128.1, 127.5, 124.1. IR (ATR) (cm⁻¹) 3189, 2923, 2852, 1617, 1552, 1486, 1458, 1423, 1360, 1257, 1213, 1118, 1072, 853, 753, 719, 696. Found: C, 71.89; H, 5.53%. Calcd for C₁₃H₁₀O₂·H₂O: C, 72.21; H, 5.59%.

Metal Ion Coordination (Typical Procedure): To a THF solution (10⁻⁵ M (1 M = 1 mol dm⁻³)) of Tp2OP was added a MeOH solution of NaOH (10⁻³ M) where the molar ratio of base relative to tropolone was kept at unity. A varying amount of CuCl₂ (MeOH solution, 10⁻³ M) was subsequently added while maintaining the volume ratio of THF/MeOH at 20/1. After shaking the solution in a vial several times, UV and PL spectra were collected.

Results and Discussion

Preparation. 5-Bromotropolone was synthesized by modifying methods¹⁵ reported earlier starting from 1,4-cyclohexadiene in four steps (See, Supporting Information, Figures S1–S4). Three different tropolone-terminated oligomeric fluorophore (Tp2OP, Tp2OPV, and Tp2OPE) bearing connecting groups were prepared by using palladium-catalyzed coupling reactions, as shown in Scheme 1. Although the tropolone unit was likely to deactivate the palladium catalyst because of the coordination ability to the metal center, the cross coupling reactions successfully proceeded to give desired products. Those ¹H NMR spectra are shown in Figures S5–S7. The configuration of C=C double bond in Tp2OPV was proven to be trans judging from the coupling constant of vinylene protons (*J* = 16 Hz). The characteristics of the C=O double bonds were dependent upon the chemical structure of the connecting group. Namely, the carbonyl stretching vibration of Tp2OP, Tp2OPV, and Tp2OPE were observed at 1619, 1611, and 1614 cm⁻¹, respectively, in the IR spectra. This trend agrees with our previous report about conjugated polymers with a tropone ring in the main chain, where the carbonyl stretching vibration of the tropolone ring embedded in the phenylenevinylene structure was observed in the lowest wave-number region.^{5b} The results of elemental analyses indicated the inclusion of a water molecule, which may be due to the intermolecular hydrogen-bonding interaction with the tropolone unit. All materials, especially Tp2OP, demonstrated good solubility in common organic solvents. Furthermore, Tp1OP bearing one tropolone ring (Figure S8) and OP without any tropolone ring (Figure S9) were synthesized as reference compounds by Suzuki coupling reaction. The carbonyl stretching vibration of Tp1OP was observed at 1617 cm⁻¹.

Optical Properties. The color of powdery Tp2OP was yellowish-green, which was much different from that of a terphenyl analog OP (colorless). The colors of Tp2OPV and Tp2OPE were red and orange, respectively. Thus the tropolone unit seems to have a significant influence upon the electronic state of the material. The UV and PL spectra of tropolone-



Scheme 1. Synthetic route of tropolone-terminated oligomeric fluorophores.

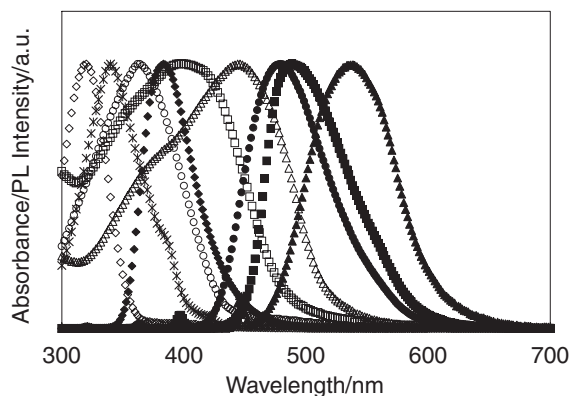


Figure 1. UV (open mark) and PL (closed mark) spectra of tropolone-terminated oligomeric fluorophores and reference compounds in THF solution (10^{-5} M) (circle: Tp2OP, triangle: Tp2OPV, square: Tp2OPE, diamond: OP, and star: Tp1OP).

terminated oligomeric fluorophores together with reference compounds were measured in a THF solution (10^{-5} M). Tp2OP showed an absorption maximum at 364 nm, which obviously red shifted as compared with that of OP (320 nm) possessing a similar three aromatic ring sequence (Figure 1). The tropolone ring has therefore a rather delocalized π -electron system. Even Tp1OP with one tropolone ring demonstrated an absorption maximum at 340 nm. Tp2OPV and Tp2OPE bearing vinylene and ethynylene connecting groups, respectively, showed absorption maxima at lower energy region (446 and 398 nm) as previously reported for other conjugated molecules. They also had smooth shoulders at 375 and 358 nm. Meanwhile, Tp2OP showed an emission maximum at 479 nm in the blue fluorescent region. The fluorescence quantum yield was determined to be 11% using quinine sulfate as a standard. In contrast, OP without any tropolone unit showed an emission maximum at 383 nm (deep blue) and the fluorescence quantum yield was 35%. Tp2OP has a polarized carbonyl group and part of the excited energy might be released through a non-radiative process by the C=O stretching vibration. The intersystem crossing of excited singlet state to triplet state is also

responsible for the low quantum yield. Tp2OP, bearing two tropolone units in the opposite direction at both termini, is nevertheless considered to be relatively less polar because the local dipole moments arising from tropolone cancel each other. It is believed however, that Tp1OP is highly polar although we could not experimentally evaluate the molecular dipole moment. Accordingly, Tp1OP did not emit light at all. Tp2OPV and Tp2OPE had emission maxima at 539 and 489 nm, respectively (Figure S10). The fluorescence quantum yield was 8% for Tp2OPE and was lower (1%) for Tp2OPV. The high or low fluorescence quantum yield of fluorophore was not affected by the Stokes shift but correlated with the connecting group between aromatic rings. The shorter triple bond in Tp2OPE produces stronger bond alternation, which increases the intrinsic band gap and is unfavorable for conjugation.¹⁶ Ring rotation around carbon–carbon triple bonds is rather more feasible than Tp2OP and Tp2OPV to release the excited energy by non-radiative process.

Subsequently, the UV and PL spectra of Tp2OP were collected in various solvents. Tp2OP could dissolve not only in apolar solvents such as THF and CHCl_3 but also in highly polar solvents such as DMF and MeOH. The large dipole moment of the tropolone ring may be a consequence of good solubility even in MeOH, which is often a poor solvent for rigid π -conjugated molecules. The UV spectra gradually red shifted as the dielectric constant of solvent increased (Figure S11). The absorption maxima in toluene and DMF were observed at 362 and 377 nm, respectively. In DMF and MeOH, broad peaks were detected at ca. 400 nm. Meanwhile, Tp2OP exhibited positive solvatochromic behavior. The PL spectra demonstrated a bathochromic shift and a good linear relationship was found between the emission maximum wavelength and the dielectric constant of solvent (Figure 2). The shift of emission maximum with increasing solvent polarity corresponds to an increase in the dipole moment, indicating the charge-transfer character of the emitting state.¹⁷ The fluorescence quantum yields in THF and DMF were 0.11 and below 0.01, respectively. It is conceivable that the central dialkoxybenzene unit and terminal tropolone unit act as electron-donor and electron-acceptor, respectively. In highly polar MeOH, the fluorescence

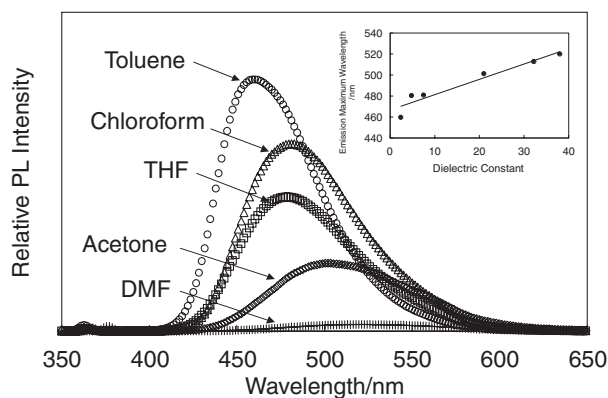


Figure 2. PL spectra of Tp2OP in various solvents (10^{-5} M) (circle: toluene, triangle: CHCl_3 , square: THF, diamond: acetone, and cross: DMF). A spectrum in NMP is omitted for clarity. The inset shows the emission maximum wavelength as a function of dielectric constant of solvent.

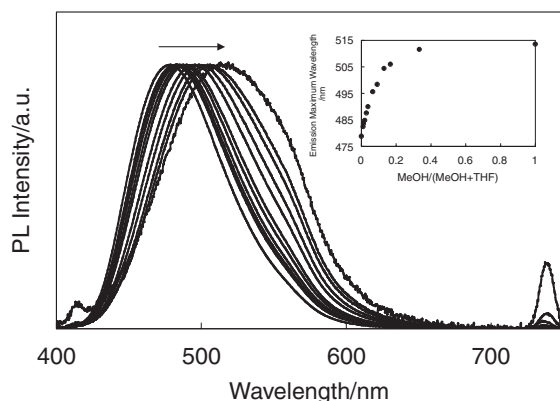


Figure 3. Change of PL spectra of Tp2OP by increasing concentration of MeOH from 0 to 50 vol % in THF. The inset shows the emission maximum wavelength as a function of MeOH content.

quantum yield of Tp2OP was almost zero, which originates from intermolecular hydrogen bonding with MeOH. When a ^{13}C NMR spectrum was measured in CDCl_3 containing ca. 30 vol % $\text{MeOH-}d_4$, the carbon signal assignable to C=O in Tp2OP shifted from 170.9 to 172 ppm. This finding actually supports the protonation of C=O by MeOH in the ground state. The PL emission behavior can be visualized in Figure S12.

To evaluate the influence of MeOH upon the optical properties of fluorophores in detail, the volume percentage of MeOH against THF was consecutively changed in the solution of Tp2OP, Tp2OPV, and Tp2OPE together with OP. Figure S13a illustrates the UV spectra of Tp2OP under various concentrations of MeOH, in which the absorption maximum wavelength shifts from 364 nm in $\text{THF/MeOH} = 100/0$ to 373 nm in $\text{THF/MeOH} = 0/100$. Tp2OPV and Tp2OPE also demonstrated red-shifts of 16 and 25 nm, respectively (Figures S13b and S13c, respectively). Although an accurate emission maximum of Tp2OPV and Tp2OPE could not be determined due to the weak fluorescence, that of Tp2OP obviously shifted from 479 to 514 nm with increasing concen-

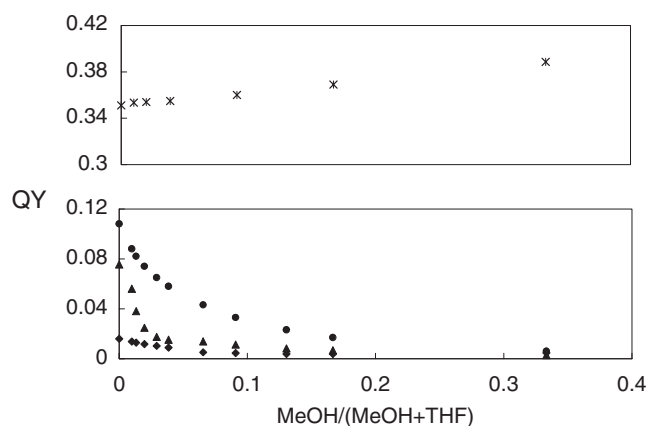


Figure 4. Fluorescence quantum yields (QYs) of fluorophores as a function of volume ratio of MeOH in THF (circle: Tp2OP, triangle: Tp2OPE, diamond: Tp2OPV, star: OP).

tration of MeOH (Figure 3). Since no detectable shifts were observed in the spectra of a terphenyl analog OP within the same range, the solvatochromic and solvatofluorochromic characteristics are ascribed to the introduction of tropolone.

The change of PL intensity of tropolone-terminated fluorophores was much different from that of OP without a tropolone ring (Figure 4). The fluorescence quantum yields (QYs) of Tp2OP, Tp2OPV, and Tp2OPE exponentially dropped and those were below 0.01 as the content of MeOH reached 30 vol %, that can be attributed to the interaction with a protic solvent (vide supra). In sharp contrast, QY of OP gradually increased. Many molecules tend to quench fluorescence in the condensed state such as film, which can be understood by the intermolecular vibronic interactions to induce nonradiative deactivation. However, unique enhanced emission rather than a fluorescence quenching in the solid state was recently reported for molecules with internal rotation around carbon-carbon bonds.¹⁸ It is assumed that this unique fluorescence change is more or less related to the effects of intramolecular planarization or a specific aggregation (H- or J-aggregation) in the solid state. OP might form nanoparticles by adding a poor solvent MeOH to induce an aggregation-induced enhanced emission (AIEE).

Metal Ion Coordination. In order to gain insights into the potential ability of tropolone-terminated fluorophores as a sensory material for metal ions, a UV titration experiment was carried out. After the deprotonation of Tp2OP by NaOH, the absorption maximum red shifted from 368¹⁹ to 402 nm. Subsequent addition of CuCl_2 until the ratio of $[\text{Cu}^{2+}]/[\text{Tp2OP}]$ reached unity, the spectra revealed a further red shift of absorption maximum peak from 402 to 412 nm as shown in Figure 5. As discussed later, it is conceivable that the ion exchange occurs from Na^+ ion to Cu^{2+} ion by adding CuCl_2 . These red shifts in the presence of metal ions may have arisen from a charge-transfer interaction between the electron-rich dialkoxybenzene unit and the electron-deficient metal-coordinated tropolone moiety. The coordination of Cu^{2+} ion was also followed by means of the IR spectrum of a material obtained under more concentrated conditions (10^{-4} M). The carbonyl stretching vibration in Tp2OP was detected at 1619 cm^{-1} ,

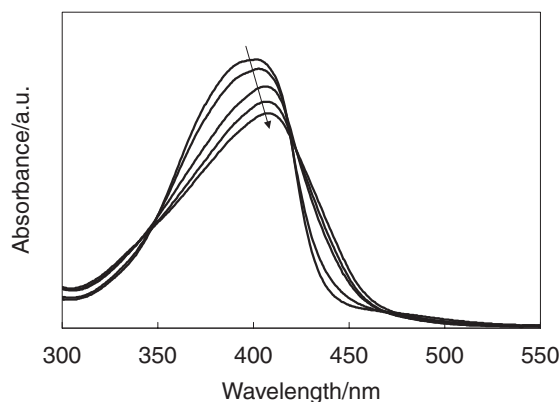


Figure 5. Change of UV spectra upon addition of CuCl_2 to Tp2OP in the presence of NaOH (2 equiv relative to Tp2OP) in THF/MeOH (20/1 by volume) (10^{-5} M). The spectra are shown at selected $[\text{Cu}^{2+}]/[\text{Tp2OP}]$ ratios ranging from 0 to 1.

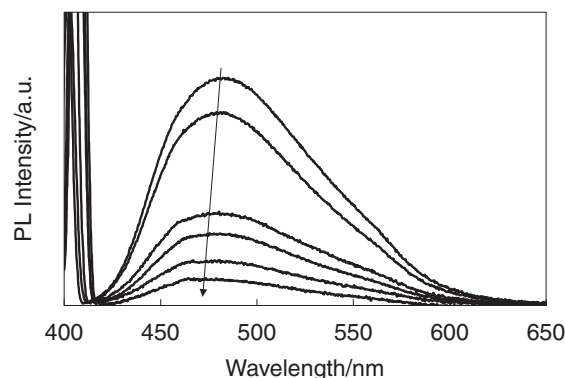


Figure 6. Change of PL spectra upon addition of CuCl_2 to Tp2OP in the presence of NaOH (2 equiv relative to Tp2OP) in THF/MeOH (20/1 by volume) (10^{-5} M). The spectra are shown at selected $[\text{Cu}^{2+}]/[\text{Tp2OP}]$ ratios ranging from 0 to 1. The excitation wavelengths were those of the absorption maximum.

Table 1. UV and PL Responses of Tp2OP upon Addition of Various Metal Ions^{a)}

	Metal-free	Na^+	Ca^{2+}	Zn^{2+}	Cu^{2+}	Al^{3+}	Fe^{3+}
$\lambda_{\text{abs}}/\text{nm}^{\text{b)}$	368	402	395	399	408	401	394
$\lambda_{\text{em}}/\text{nm}^{\text{c)}$	489	485 (m)	518 (m)	502 (m)	470 (w)	479 (m)	484 (w)

a) Conditions: THF/MeOH = 20/1 by volume. The concentrations of metal ion $[\text{metal ion}]/[\text{Tp2OP}]$ were 2 for monovalent ion, 1 for divalent ions, and 2/3 for trivalent metal ions, respectively. b) The absorption maximum. c) The emission maximum. The characters in parenthesis indicate relative PL intensity compared to metal-free Tp2OP (m: middle and w: weak).

which shifted to 1601 cm^{-1} by forming the complex with Cu^{2+} ion (Figure S14).

Metal ion coordination was also confirmed by the change of emission behavior as was evident from the PL spectra observed upon the addition of CuCl_2 into a solution of Tp2OP. The emission maximum wavelength blue shifted from 485 nm^{20} to approximately 470 nm and spontaneously a remarkable decrease of the PL intensity was observed (Figure 6). The fluorescence emission gradually decreased until the molar ratio of $[\text{Cu}^{2+}]/[\text{Tp2OP}]$ reached unity, and beyond this point, a fluorescence signal almost vanished. The intrachain energy transfer to the electron-deficient metal-coordinated tropolone moiety came about to effectively quench the fluorescence emission.²¹

Finally, the metal ion coordination to Tp2OP was likewise carried out for other divalent ions (Ca^{2+} and Zn^{2+}) and trivalent ions (Al^{3+} and Fe^{3+}). The ionochromic responses of Tp2OP with these metal ions are summarized in Table 1 in conjunction with the results of Na^+ and Cu^{2+} ions. The absorption maximum always red shifted as compared with that of metal-free Tp2OP. The magnitude of shift was independent of the valence number of ions as there was no great difference between Ca^{2+} and Fe^{3+} (ca. 5 nm) or Zn^{2+} and Al^{3+} (ca. 10 nm). Chelate complex coordinated with Fe^{3+} and Cu^{2+} ions showed the shortest and longest absorption maximum wavelength, respectively. The coordination of Fe^{3+} ion also demonstrated a shoulder at ca. 473 nm . The ion responsive property of Tp2OP was confirmed more remarkably from the PL spectra as illustrated in Figure 7. According to the

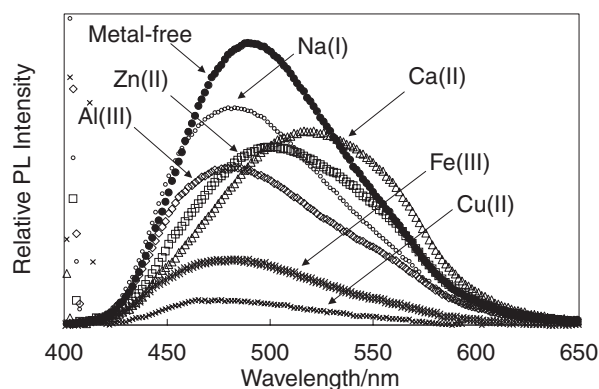


Figure 7. Change of PL spectra upon addition of various metal ions to Tp2OP in THF/MeOH (20/1 by volume) (10^{-5} M) (closed circle: metal-free, open circle: Na^+ , triangle: Ca^{2+} , square: Zn^{2+} , diamond: Al^{3+} , star: Fe^{3+} , and cross: Cu^{2+}). The concentrations of metal ion $[\text{metal ion}]/[\text{Tp2OP}]$ were 2 for monovalent ion, 1 for divalent ions, and 2/3 for trivalent metal ions, respectively.

spectroscopic influence of metal ion upon the emission property of Tp2OP, the metal ions can be categorized into two groups. The first group causes red-shift of the fluorescence spectra, which includes typical element such as Ca^{2+} and Zn^{2+} ions. The PL intensity of these materials was moderate. The second group conversely induces blue-shift of the fluorescence spectra, which includes Cu^{2+} , Al^{3+} , and Fe^{3+} ions. The coordination with transition-metal ions (Cu^{2+} and Fe^{3+})

substantially quenched fluorescence signals that could not be seen. The difference in the PL spectra may be a consequence of the following two factors. One is the ability of metal ions to substitute pre-coordinated Na^+ ion generated by the addition of NaOH to Tp2OP. The complete substitution is believed to cause the drastic change of PL spectra. Another can be attributed to electron density variations on the fluorophore, caused by introducing positively charged metal ions. It is noted that Tp2OP has a potential ability to bind not only transition-metal ions but also alkali and alkaline earth metal ions.

Conclusion

We have prepared three tropolone-terminated oligomeric fluorophores and revealed optical properties. The new fluorophore has a widespread conjugated system and demonstrated interesting optical response to solvent polarity. The addition of metal ion to the tropolone unit brought about the formation of chelate complexes and their optical spectra were dependent upon the nature of the metal ions.

This work was financially supported by Iketani Science and Technology Foundation (ISTF). We also thank Ms. Yachiyo Taniyama for elemental analyses.

Supporting Information

Synthetic procedures and ^1H NMR spectra of 5-bromotropolone and reference compounds. ^1H NMR spectra of fluorophores. UV spectra and light-emitting behavior of fluorophores. IR spectra of metal-free and metal-coordinated fluorophores. This material is available free of charge on the web at <http://www.csj.jp/journals/bcsj/>.

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