Multicolor Fluorescent π-Conjugated Oligomer Having Salicylideneaniline Moieties

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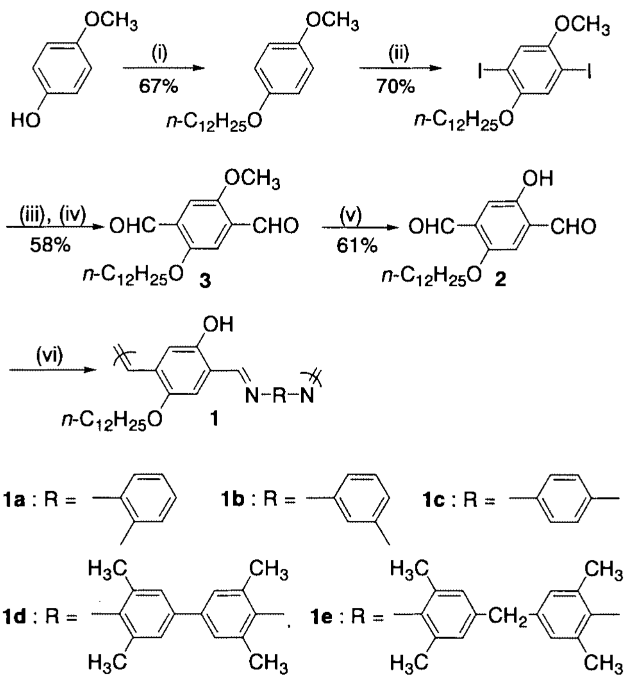
A multicolor luminescence active π-conjugated oligomer, in which the emission color can be controlled by changing the wavelength of the excitation light, was synthesized by the condensation of 1,2-phenylenediamine with 5-dodecyloxy-2-hydroxyterephthalaldehyde.

The fluorescence of molecules originates from the decay process from the singlet excited state to the ground state, and if the emission is sufficiently strong and appears in the visible region, such fluorescent molecules are applicable as light-emitting materials. Since the luminescence is readily detected even by the naked eye, fluorescent molecules are utilized as sensors, displays, probes and so on. In the present study, we synthesized a new π-conjugated oligomer having salicylideneaniline moieties in the main chain and found that its emission color changes from green to yellow, and in addition, to red-orange, by changing the wavelength of the irradiation light, that is, by simply varying the photoexcitation energy.

The target molecule (**1a**) is an oligomer prepared by the condensation of 5-dodecyloxy-2-hydroxyterephthaldehyde (**2**) with *o*-phenylenediamine (Scheme 1). The incorporation of a dodecyloxy group is to enhance the solubility of **1a** because the aromatic polyazomethines generally show very poor solubility. The introduction of a hydroxy group at the ortho position to the formyl group of **2** is to allow the oligomer **1a** to undergo excited-state intramolecular proton transfer (ESIPT).[1] ESIPT is a photochemically induced tautomerization process of molecules having a cyclic hydrogen bond. Photochemical excitation of the ground state of such molecules is followed by an extremely rapid tautomerization process (keto–enol tautomerization) to give energetically more stable excited-state tautomers. The tautomers radiatively or nonradiatively relax to the metastable ground state which is then thermally converted to the normal form. If the relaxation of the excited-state tautomers is accompanied with a radiation process, fluorescence with a large Stokes shift is attainable. Therefore, the loss of the emission energy by the reabsorption of the emitted fluorescence photons can be reduced.

Scheme 1 shows the synthetic route to the monomers (**2** or **3**) and the oligomer (**1**).[3] The synthesis of monomer **2** involves the alkylation of 4-hydroxyphenol, iodination of the 2- and 5-positions of the aromatic ring, formylation of the C–I bonds, and the removal of the methyl group in the presence of LiCl in *N*,*N*-dimethylformamide.[4] The oligomerization was conducted in a mixed solvent (hexamethylphosphoramide and *N*-methyl-2-pyrrolidinone) in the presence of LiCl as a condensation agent.[2] Orange-colored oligomer **1a** was obtained in 49% yield as a methanol/water insoluble part, and its molecular weight and polydispersity estimated by GPC (polystyrene standards) were 1690 and 1.60, respectively.

Scheme 1.



(i) n-$C_{12}H_{25}Br$, NaOH, DMF, 170 °C, 15 h. (ii) I_2, KIO_4, AcOH, H_2SO_4, H_2O, 80 °C, 17 h. (iii) n-BuLi, Et_2O, –78 °C, 30 min. (iv) DMF, rt, 30 min, then H_3O^+. (v) LiCl, DMF, 160 °C, 20 h. (vi) Diamine, NMP, HMPA, LiCl, rt, 24 h.

Oligomer **1a** displayed very unique fluorescence behavior. As shown in Figure 1a, the UV–visible spectrum exhibited a broad absorption with two major peaks around 310 and 360 nm. When **1a** was excited by UV light (360 nm) in THF, four fluorescent peaks were observed at 390, 418, 440, and 527 nm.[5] Because the former three peaks do not significantly contribute to its luminescence color, the fluorescence with a maximum centered at 527 nm corresponded to the green emission that was clearly recognized by the naked eye. Irradiation at 390 nm gave three emission peaks at 418, 440, and 517 nm, similarly to the photoirradiation at 360 nm. However, a shoulder was detected at 558 nm in the emission peak in the visible region (470–700 nm). This slight spectral difference caused a drastic change in the emission color. Namely, irradiation at 390 nm results in yellow emission. Emphasis should be placed on the fact that the further decrease in the photoexcitation energy to 420 nm provided red-orange emission with a fluorescent peak centered at 576 nm. Figure 2 clearly demonstrates the fluorescence color variation upon manipulation of the photoexcitation energy: green, yellow, and red-orange colors are readily

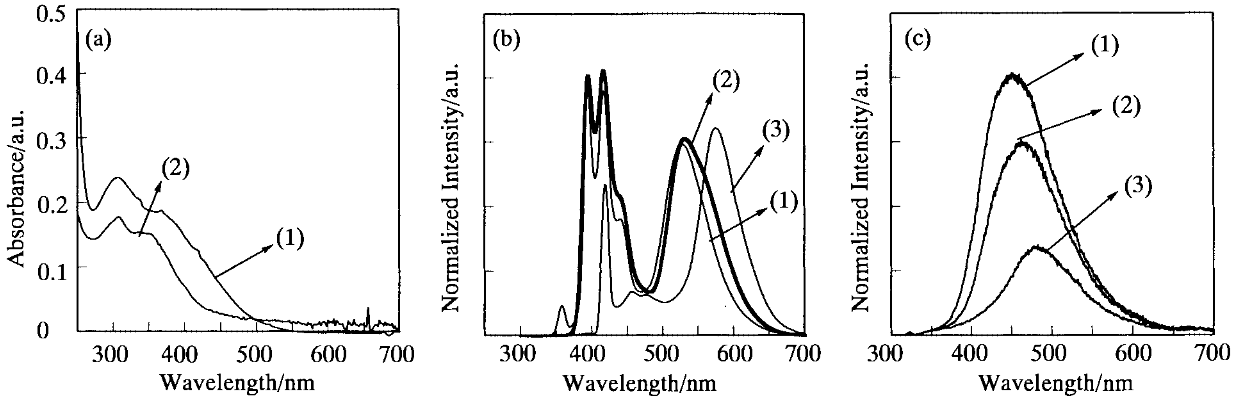
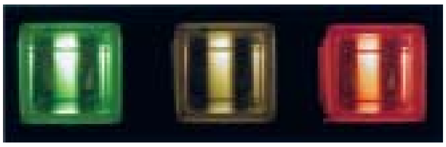


Figure 1. (a) UV-visible spectra of **1a** (1) in THF and (2) in the solid state, (b) fluorescence spectra of **1a** upon the excitation at (1) 360, (2) 390, and (3) 400 nm in THF, and (c) fluorescence spectra of **1a** upon the excitation at (1) 380, (2) 400, and (3) 420 nm in the solid state.

obtained simply by changing the wavelength of the irradiation light. The quantum yields of photoluminescence of oligomer **1a** in THF were 8.5, 7.9, and 2.1% for green, yellow, and red-orange emissions, respectively. A similar dependence of emission color on the photoexcitation energy was observed in toluene and $CHCl_3$. The emission color also varied in the solid state (Figure 1c). The excitation of the film of **1a** at 380 and 420 nm resulted in green and red-orange emissions, respectively.



(a) (b) (c)

Figure 2. Fluorescence of oligomer **1a** upon the excitation at (a) 360, (b) 390, and (c) 400 nm in THF.

Analogous polymers (**1b**, **1c**) were also prepared using *m*- and *p*-phenylenediamines as monomers in 98 and 92% yields respectively. These polymers were partly soluble in organic solvents, and the soluble oligomeric part (M_n = 3170 for **1b**, 3890 for **1c**) showed emission in quantum yields of 0.11 and 0.058%, respectively. In contrast to oligomer **1a**, there was no dependence of the emission wavelength on the photoexcitation energy: only orange color was observed from both oligomeric parts irrespective of the irradiation energy. In a similar way, soluble, high molecular weight polymers, **1d** (M_n = 11800, 92% yield) and **1e** (M_n = 7900, 92% yield), were prepared by the condensation with 3,3',5,5'-tetramethylbenzidine and bis(4-amino-3,5-dimethylphenyl)methane, respectively. These polymers displayed orange emission with maximum around 590 nm, which did not change upon variation of the excitation wavelength. Thus, ortho-substitution at the diamine moieties appears to contribute to the multicolor emission. The presence of a hydroxy group was indispensable for generation of the emission because the soluble part of oligomer **4** (M_n = 3120) prepared from **3** and *p*-phenylenediamine in 93% yield was fluorescence inactive. All of the oligomers and polymers **1** having a hydroxy group on the aromatic rings showed very large Stokes shift. For example, the Stokes shifts of the visible emission for oligomers and polymers **1b**–**1e**, were ca. 200 nm. Since the absorption corresponding to the visible emission cannot be completely assigned at present, the Stokes shift cannot be estimated for **1a**. However, a very large Stokes shift can be recognized by the fact that the red-orange emission of **1a** does not overlap with its UV absorption. These findings suggest that the emission originates from the radiation process from the excited-state proton-transferred tautomer to its metastable ground state.[1]

In summary, we demonstrated a new photoluminescent organic π-conjugated oligomer that emits multicolor light controllable by changing the photoexcitation energy. As shown in Figure 1, oligomer **1a** exhibits very broad absorption and complicated emission peaks. Thus, **1a** is likely to compose plural fluorescent segments with different structures, which is also suggested by the observation of poorly resolved ^{1}H NMR resonances of **1a**. The results presented in this study indicate that energy transfer between the fluorescent segments is slow or does not occur. This result differs from the general feature of fluorescence, namely, that the emission predominantly originates from the lowest band due to the rapid energy transfer between lumophores. Further investigation to clarify the origin of the multicolor emission is now in progress.

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References and Notes

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3 The structure of the oligomers in Scheme 1 was used only for simplicity. The oligomers probably contains both head-to-tail and head-to-head structures with respect to the unit from the dialdehyde.
4 A. M. Bernard, M. R. Ghiani, P. P. Piras, and A. Rivoldini, *Synthesis*, **1989**, 287 (1989).
5 Excitation at 310 nm gave a similar emission spectrum.