

Molecular Design for Luminescent Azobenzene-Containing Conjugated Polymers and Their Application to Film Sensors for Recording Acid Exposure History

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Key words: Azobenzene; Luminescence; Conjugated polymer; Excited state intramolecular proton transfer; Density functional theory

Abstract

It has been found that azobenzene structures show luminescence by suppressing their photoisomerization and alternating electronic states through molecular modification and metal complexation. Herein, we propose the three-step design strategy for creating luminescent azobenzene derivatives from quantum chemical calculations. First, we introduced intramolecular hydrogen bonding between *o*-hydroxy groups and azobenzene moiety not only for stabilizing n-orbital of azobenzene but also for suppressing photoisomerization. Second, the expansion of the π -conjugation was employed to convert the S_0 – S_1 transition to the allowed π – π^* transition. Third, we derived the fast excited-state intramolecular proton transfer (ESIPT) process which is suitable for observing emission from azobenzene. Through these steps, we designed and synthesized azobenzene derivatives and succeeded in observing intense deep-red to NIR emission from conjugated polymers including azobenzene moieties in the main chain. Furthermore, we applied the synthesized polymers to film-type acid vapor sensors. In addition to the real-time detection ability toward acid vapor observed in our previous work, we found that the current material can discriminate whether the film was once exposure to acid vapor from the changes in luminescence and film colors. Our findings reveal that azobenzene is a potential platform for creating luminescent materials with stimuli-responsiveness according to rational molecular design.

1. Introduction

Azobenzenes have been applied in a wide range of fields such as dyes, cosmetics and pH indicators.^[1,2] Recently, the azobenzene skeleton has attracted interest as a key unit for constructing smart materials because of its unique features such as *cis*-to-*trans* photoisomerization.^[3–5] It is well known that *trans*-to-*cis* isomerization takes place in the excited state of azobenzene when the molecule is irradiated by ultraviolet light which corresponds to the energy gap of the π - π^* (S_0 - S_2) transition (300–400 nm). Meanwhile, *cis*-to-*trans* photoisomerization can be thermally activated in the ground state or photochemically induced within the picosecond lifetime by blue light which corresponds to the energy gap of n - π^* (S_0 - S_1) transition (>400 nm). Owing to these unique features, azobenzenes have been also utilized to construct functional materials, such as liquid crystals^[6,7], magnetic materials^[8] and biomaterials^[9,10].

It is also known that azobenzene derivatives have been rarely used as luminescent materials because the excitation energy is critically consumed through the fast non-emissive deactivation process accompanied by *cis*-*trans* photoisomerization.^[11–13] So far, emission from azobenzene derivatives has been observed based on the concept of suppressing the *cis*-*trans* photoisomerization under limited conditions, such as in a rigid matrix at low temperature.^[14–17] Recently, Kawashima and coworkers have made breakthrough reports that boron-substituted azobenzene compounds exhibited intense emission.^[18–20] They proved that the boron coordination to the azobenzene moiety can convert the π - π^* transition into the S_0 - S_1 transition by stabilizing the n -orbital involved in the azobenzene moiety. Furthermore, we revealed that element-fused azobenzene complexes can be used for the monomer of conjugated polymers showing highly-efficient near-infrared (NIR) emission through dramatical stabilization of the energy level of the

lowest unoccupied molecular orbital (LUMO).^[21–35] We also proposed that azobenzene can be regarded as a conjugated monomer in which a carbon–carbon double (C=C) bond in stilbene is replaced by a nitrogen–nitrogen double (N=N) bond. Based on this idea, we have shown that azobenzene can provide conjugated systems with narrower energy gaps than stilbene.^[36,37]

Herein, we developed luminescent azobenzene derivatives by *o*-hydroxylation with azobenzene according to the three-step design strategy. Based on the idea that the formation of hydrogen bonds between hydroxy groups and azobenzene moiety not only interlocked the structure but also convert the π – π^* transition of azobenzene into S_0 – S_1 transition, similarly to boron coordination, we observed that luminescent azobenzene derivatives can be obtained by *o*-hydroxylation.^[38–41] Furthermore, we expanded the scopes of our research to the conjugated polymers to improve the photophysical properties and film-formability.^[42–45] We found that emission color can be tuned by selecting comonomer units. In addition, as an application, we evaluated stimuli responsiveness of the polymers as a film-type acid vapor sensor. In our previous report, we developed reversible, real-time, and reusable acid vapor sensor polymer films according to protonation on a nitrogen atom in azobenzene moieties.^[46] In this research, the films can record information on whether the film has been exposed once to acid based on deprotection of protected groups by acid vapor (Figure 1). We confirmed that the elimination of the protecting groups should be a trigger for this recording property.

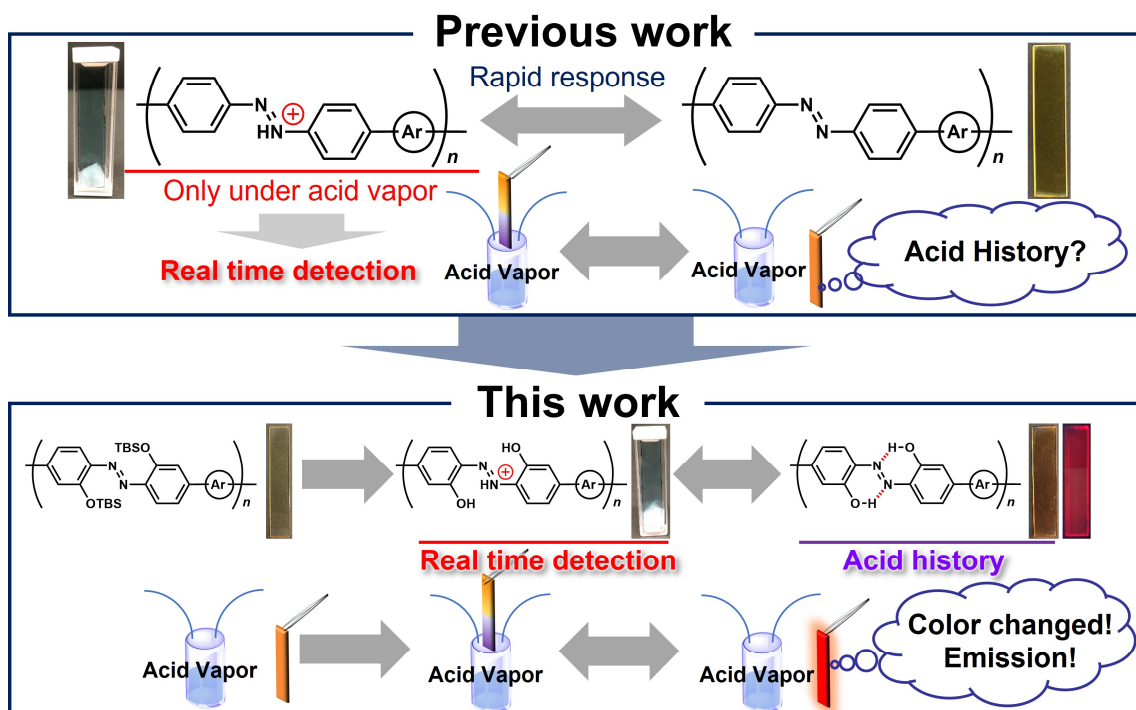


Figure 1. Illustration of comparison of acid vapor sensor films between previous work and this work.

2. Results and Discussion

2.1 Molecular design

To develop emissive azobenzene derivatives, we introduced hydroxy groups at the *ortho* position of azobenzene based on three presumptions. The concept of molecular design are illustrated in Figure 2. First, we employed the *o*-hydroxylated structure to suppress the *trans*-to-*cis* photoisomerization. It is well known that the energy associated with the excited state is predominately used for photoisomerization rather than emission. Therefore, it is essential to prohibit the *trans*-to-*cis* photoisomerization in the excited state. We presumed that the azobenzene structure should be locked in the *trans* conformation

by intramolecular hydrogen bonding between the phenolic hydroxy group and nitrogen atom, which may minimize the *trans*-to-*cis* photoisomerization and subsequently inhibit the rapid thermal relaxation process.^[47–49] The similar effect derived from intramolecular hydrogen bonding was also observed in *o*-aminated azobenzene derivatives.^[50,51]

The second problem concerns the rules of electronic transitions in azobenzene. In general, fluorescence is obtained accompanied with energy relaxation from the lowest excited state (S_1) to the ground state (S_0) after fast internal conversion from the S_i to S_1 states (Kasha's rule).^[52] Therefore, it is critical in fluorescent molecules that the S_0 – S_1 transition is assigned to allowed transition for presenting intense emission. Whereas, in azobenzene (**mono 0**), it has been widely recognized that the S_0 – S_1 transition is assigned to forbidden n – π^* transition and the S_0 – S_2 transition is assigned to allowed π – π^* transition. Hence, it is necessary that the S_0 – S_1 transition should be converted into allowed one. To fulfill this request concerning electronic transitions, we focused on molecular orbitals (MOs) and the transitions of **mono 0**, **mono 1** and **mono 2**. We performed density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations at (TD-)B3LYP/6-31+G(d,p) level of theory (details are shown in the Supporting information), and the distributions of the MOs and energy levels of each orbital were surveyed (Figures 3a and S1). In **mono 0**, the highest occupied molecular orbital (HOMO) is assignable to n -orbital. It should be emphasized that the *o*-hydroxy substitutions can drastically stabilize the energy levels of the n -orbitals (**mono 1**: HOMO–1, **mono 2**: HOMO–3, HOMO– m denote the $(m+1)$ th highest occupied orbital). Since there is the large contribution of the lone pairs of nitrogen atoms at the azobenzene moiety to the construction of the n -orbital, the n -orbital is highly stabilized by the interaction between hydrogen atoms and lone pairs of the nitrogen atoms.^[18] This phenolic hydroxy

substitution effect is also observed in fluorescent polyimide reported by Ando and coworkers.^[53,54] Next, we focused on HOMO-1 of **mono 0** composed of π -orbital. It is revealed that the π -orbital is destabilized to HOMO in **mono 1** and **mono 2** as n-orbital is stabilized. Moreover, π -orbital is destabilized energetically as hydroxy groups are introduced. On the other hand, the lowest unoccupied molecular orbital (LUMO) of **mono 0** is assignable to π^* -orbital, which is stabilized energetically by introducing hydroxy groups. Despite these modifications, all S_0 - S_1 transitions in **mono 0**, **mono 1**, and **mono 2** were still assigned as forbidden n- π^* transition (Figure 3b and Tables S1-S3). To convert the S_0 - S_1 transition into the allowed transition, we introduced further substitutions to *o*-hydroxy derivatives.

We designed **2_fluo'** and **2_bith'** as emissive candidates, which are introduced fluorene and bithiophene widely known as conjugated molecules at the 4,4' positions of 2,2'-dihydroxyazobenzene (**mono 2**), respectively. To obtain information on the effect of *o*-hydroxylation, we also designed **0_fluo'** and **0_bith'** as model compounds. The energy levels and transitions of these molecules are shown in Figures 4, S2-S5, and Tables S4-S7. Consequently, it is shown that the expansion of π -conjugation observed in **mono 0** to **0_fluo'** and **0_bith'** can contribute to significant destabilization of the energy levels of π -orbitals. By *o*-hydroxylation, n-orbitals and π^* -orbitals of **2_fluo'** and **2_bith'** are stabilized compared to **0_fluo'** and **0_bith'**, respectively. Significantly, the S_0 - S_1 transition in **0_fluo** and **0_bith** are assigned to n- π^* , meanwhile the S_0 - S_1 transition in **2_fluo** and **2_bith** are assignable to the allowed π - π^* transition (Figure 4). Previously, the modulation of the energy levels of the n and π -orbitals by introducing the substitutions has been performed to adjust the bandgap of the S_0 - S_1 and S_0 - S_2 transitions to improve the photoisomerization properties.^[55,56] Our results imply that by adjusting the energy

levels of n and π -orbitals, we accomplished to convert the S_0 – S_1 transition into π – π^* transition favorable for obtaining luminescence without metal complexation.

Third, we expected that emission from different emissive species, excited state intramolecular proton transfer (ESIPT) emission^[57,58], could be obtained from the 2-hydroxyazobenzene structure. ESIPT is a photochemical process that produces a tautomer with a different electronic structure from the original excited form. Since ESIPT generally takes place in an extremely faster photophysical process (fs order) compared to the photoisomerization process (ps order), emission from ESIPT process could avoid the influence of non-radiative decay derived from photoisomerization. In fact, ESIPT phenomena have been observed from 2-hydroxyazobenzene derivatives.^[59–62] However, emissions quantum yields are low. In addition, although there are several reports that 2-hydroxyazobenzene derivatives have been utilized as luminescent materials, ESIPT was not mentioned.^[38–41] In the 2-hydroxyazobenzene structure, it is possible to form both enol and keto structures in excited state (Figure 5). Therefore, we analyzed the properties of both normal and tautomer forms in those molecules based on DFT calculations (Figures S6–S9 and Tables S8–S11). It is worth noting that the S_0 – S_1 transition in **mono 1K** (keto form of **mono 1**) and the S_0 – S_1 transition in **mono 2K** (keto form of **mono 2**) are assigned to n– π^* and π – π^* transitions, respectively. Therefore, emission from the normal form and tautomer form of **mono 1** should be very weak, whereas significant emission from the tautomer form of **mono 2**, that is, **mono 2K** can be expected. Similarly, S_0 – S_1 transitions of **2K_fluo** (keto form of **2_fluo**) and **2K_bith** (keto form of **2_bith**) are assigned to π – π^* transition. Based on the above three speculations, we designed molecules and investigated the photophysical properties to prove the validity of our idea.

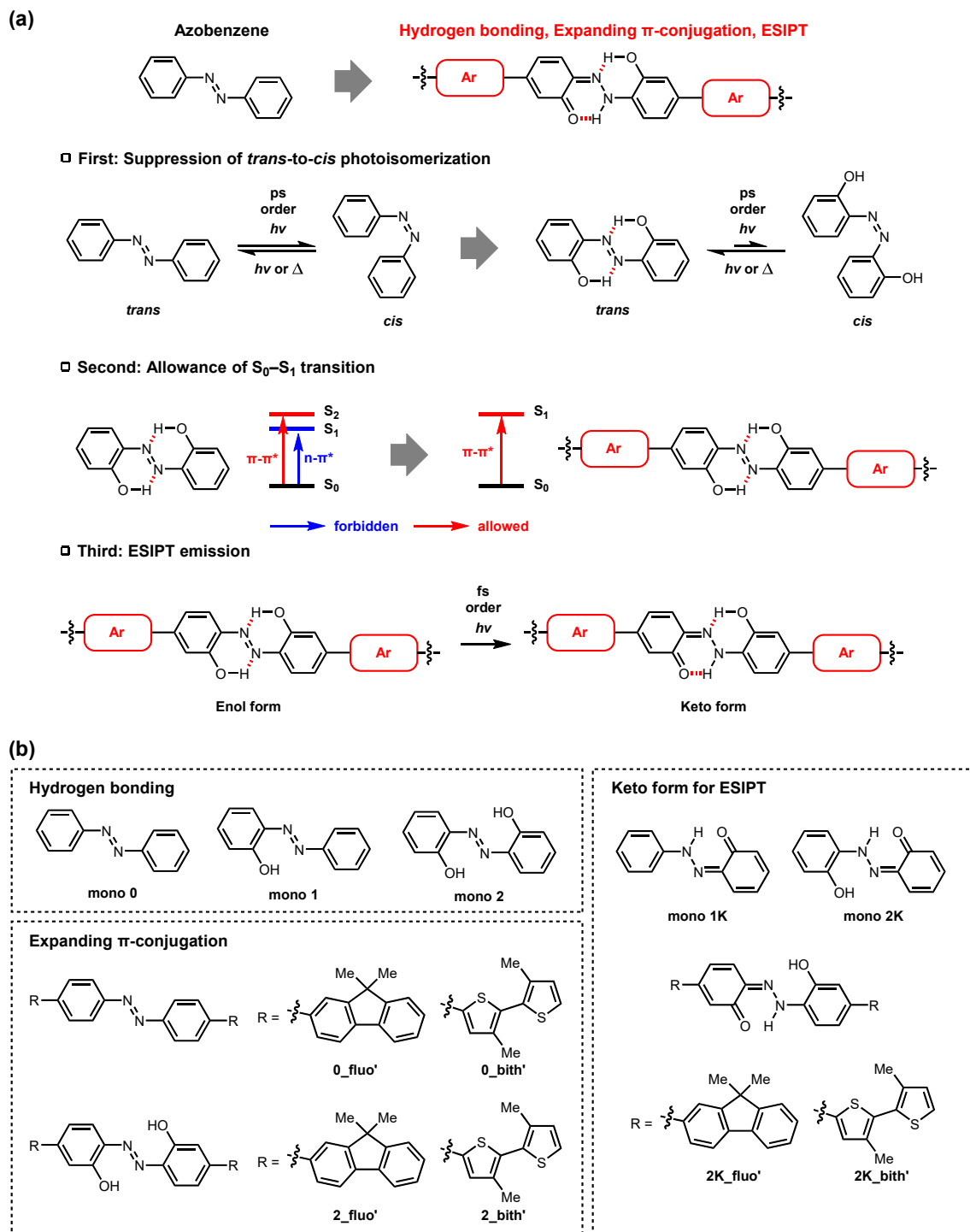


Figure 2. (a) Outline of three-step molecular design for developing emissive azobenzene derivatives. (b) Chemical structures used in DFT calculations.

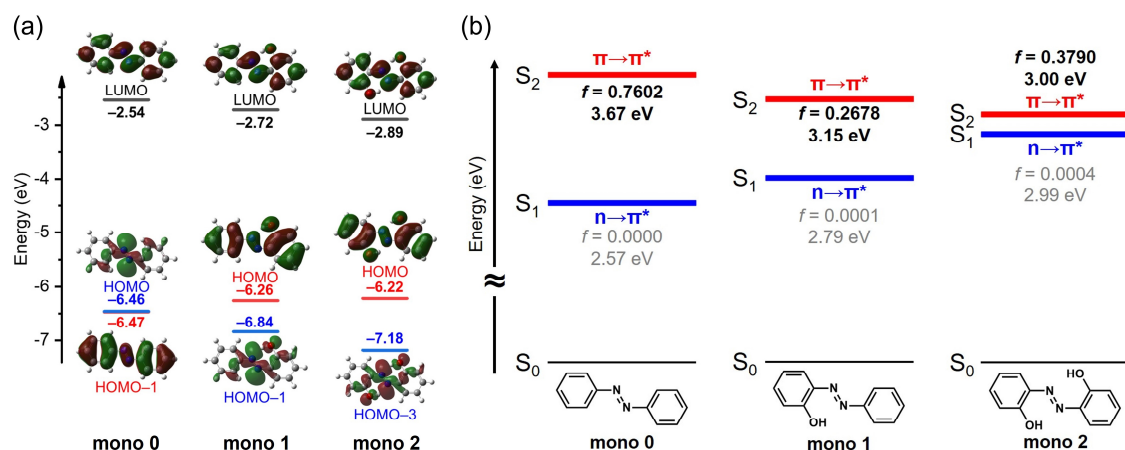


Figure 3. (a) Selected MOs and the energy levels of **mono 0**, **mono 1**, and **mono 2** obtained from DFT calculations at B3LYP/6-31+G(d,p) level (isovalue = 0.02). The n, π and π^* -orbitals are depicted in blue, red and black, respectively. (b) Results of representative transitions of **mono 0**, **mono 1**, and **mono 2** obtained from TD-DFT calculations at the TD-B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) level.

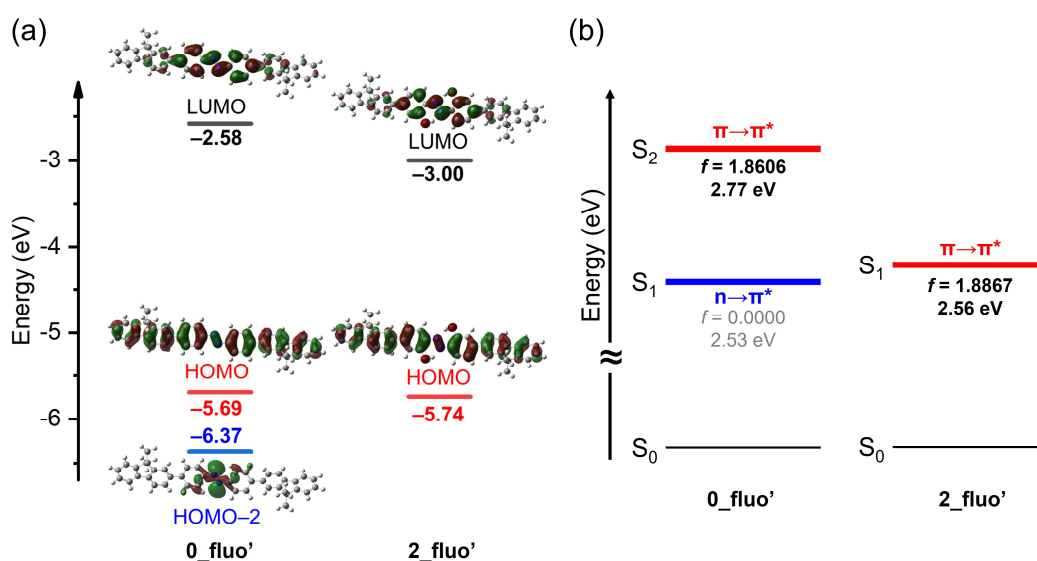


Figure 4. (a) Selected MOs and the energy levels of **0_fluo'** and **2_fluo'** obtained from DFT calculations at B3LYP/6-31+G(d,p) level (isovalue = 0.02). The n, π and π^* -orbitals are depicted in blue, red and black, respectively. (b) Results of representative transitions of **0_fluo'** and **2_fluo'** obtained from TD-DFT calculations at the TD-B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) level.

ESIPT process

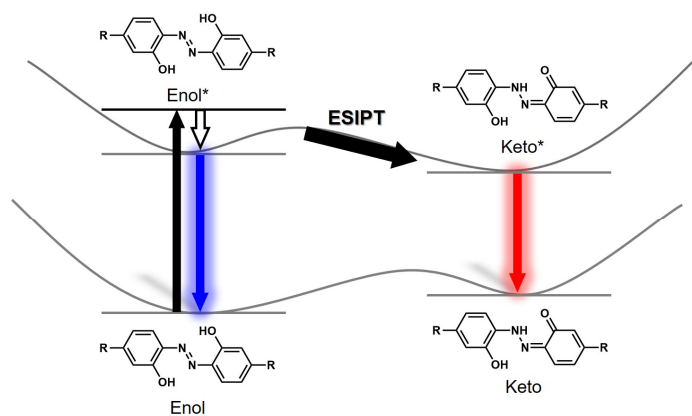


Figure 5. Schematic illustration of the ESIPT process in the 2-hydroxyazobenzene structure.

2.2 Synthesis

First, we synthesized azobenzene derivatives according to the molecular design (Scheme 1). The detailed synthetic procedures of **0_fluo**, **0_bith**, **2_fluo**, and **2_bith** are also shown in the Supporting Information. We prepared azobenzene derivatives **2** and **4** through oxidation coupling reactions.^[35,63] Subsequently, compound **6** was obtained *via* the conversion from the methoxy groups to *tert*-butyldimethylsilyl (TBS)^[64,65] protected group. Next, we performed Migita–Kosugi–Stille cross-coupling reactions^[66,67] in toluene in the presence of 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos) and Pd₂(dba)₃ (dba = dibenzylideneacetone) to connect the azobenzene units with fluorene (**8**) or bithiophene (**11**), and **0_fluo**, **0_bith**, **9**, and **12** were obtained. Since in the presence of phenolic hydroxy groups, the coupling reactions hardly progressed, we introduced the TBS groups. After the coupling reactions, the TBS groups in **9** and **12** can be easily deprotected through the treatment with trifluoroacetic acid (TFA) to afford **2_fluo** and **2_bith**, respectively. We also prepared compounds **14** and **15** with methoxy methyl (MOM) protecting groups instead of the TBS groups (Scheme 2). Similarly to **9** and **12**, we observed that **14** and **15** were converted into **2_fluo** and **2_bith** by TFA in high yields (>90%), respectively.

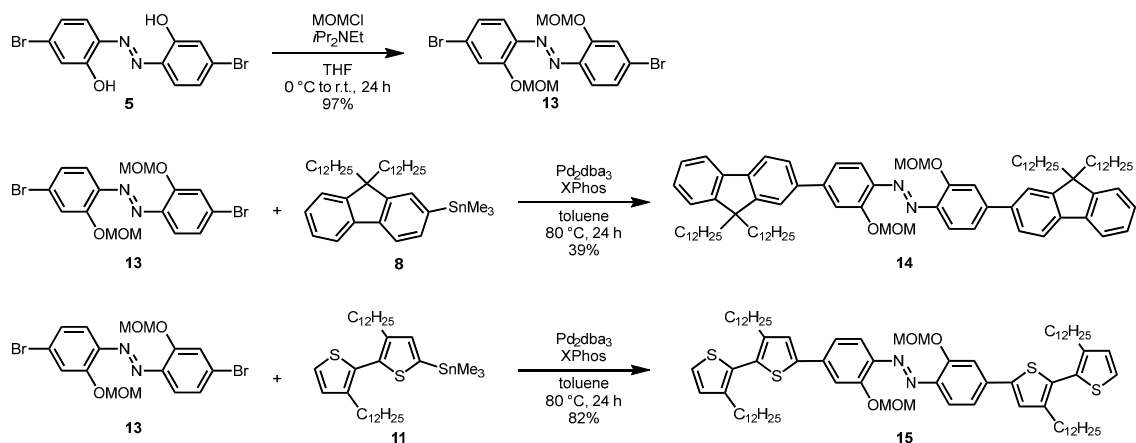
To expand the variety of electronic structures and improve film-formability, we synthesized conjugated copolymers consisting of 2,2'-dihydroxyazobenzene unit and fluorene or bithiophene unit (Schemes 3). We also prepared the polymers having protection groups (**TBS_fluo**, **MOM_fluo**, **TBS_bith** and **MOM_bith**). Polymerizations were performed with Migita–Kosugi–Stille cross-coupling reactions with respective comonomers. Reactivity in the deprotection was checked with the polymers in TFA solutions. In the cases of **MOM_bith** and **TBS_bith**, however, resulting polymers were

immiscible to most organic solvents, and the desired polymer (**2p_bith**) was not obtained. In the case of **MOM_fluo**, deprotection incompletely progressed even if the reaction time was extended or the equivalence of TFA was increased. Instead, **TBS_fluo** was fully deprotected and subsequently **2p_fluo** was successfully obtained. From ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, we confirmed that the peak derived from the TBS protecting groups were completely removed.

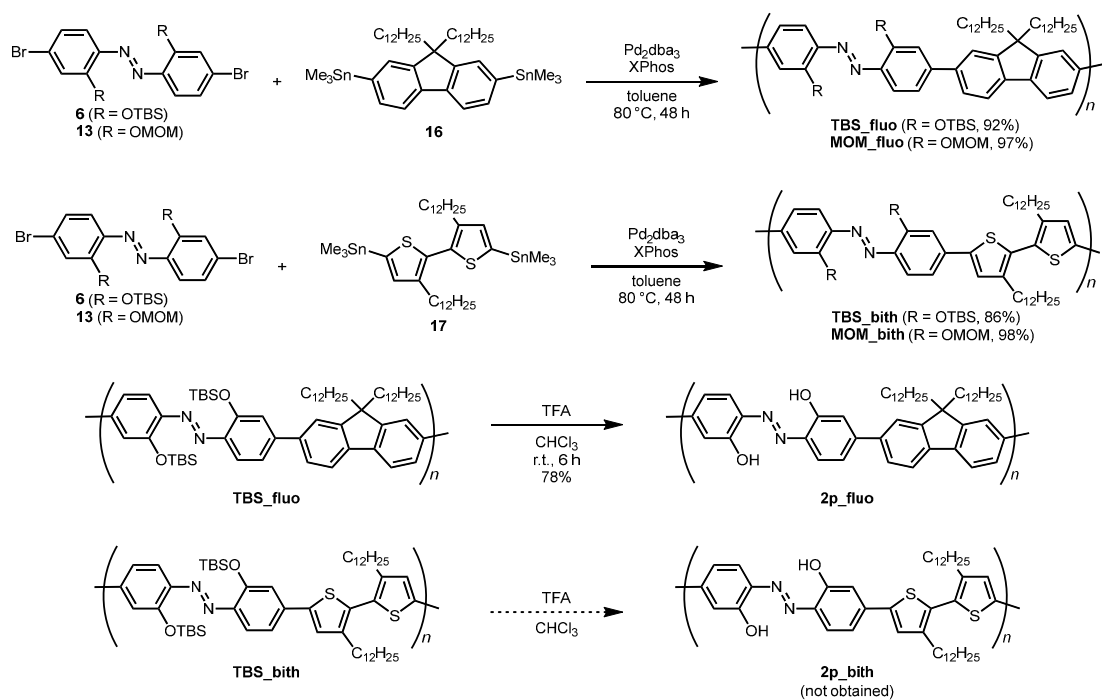
The structures of all synthesized monomers and polymers were characterized by ^1H , $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, mass spectrometry, and elemental analysis (Charts S1–S35). The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of polymers were determined by a gel permeation chromatography (GPC) with CHCl_3 as an eluent with polystyrene standards. Additionally, the polymers were fractionated on a recycling preparative high performance liquid chromatography (HPLC) to investigate the effect of molecular weight on optical properties (Figure S10 and Tables S12–S16).

It should be noted that the ^1H NMR signals from the phenolic hydroxy hydrogen atom in 2-hydroxyazobenzene derivatives were significantly detected in the downfield region over 12 ppm (**mono 1**: 12.90 ppm (in CDCl_3 , Chart S36), **mono 2**: 12.20 ppm (in CD_2Cl_2 , Chart S37), **2_fluo**: 12.45 ppm (in CD_2Cl_2 , Chart S11), **2_bith**: 12.42 ppm (in CD_2Cl_2 , Chart S13), and **2p_fluo**: 12.46 ppm (in CD_2Cl_2 , Chart S33). These data mean that the hydrogen bonds should be formed in these molecule.





Scheme 2. Chemical structures of **14** and **15**.



Scheme 3. Synthetic schemes of azobenzene polymers.

2.3 Experimental properties of azobenzene derivatives

To evaluate the validity of the molecular design for the development of the above-mentioned luminescent azobenzene derivatives, we investigated the electronic and optical properties of the synthesized compounds. First, cyclic voltammetry (CV) analysis was performed to estimate the MO energy levels and verify the validity of the DFT calculation data (Figures 6 and S11, Table S17). The LUMO energy levels were calculated from the onset of the reduction curve^[68,69] as shown in Figure S12. MO energy levels obtained from DFT calculations are listed in Figures S13–S15. Accordingly, it was shown that the introduction of hydroxy groups from **mono 0** to **mono 2** lowered the energy levels of π^* -orbitals and elevated those of π -orbitals (Figure S13). In addition, the expansion of π -conjugation from **mono 0** to **0_fluo** and from **mono 0** to **0_bith** raised the energy levels of π -orbitals and lowered those of π^* -orbitals (Figures S14 and S15). Furthermore, the introduction of hydroxy groups significantly stabilized the energy levels of π^* -orbitals according to the comparisons between **0_fluo** and **2_fluo** and **0_bith** and **2_bith**, while the energy levels of π -orbitals were relatively maintained. These trends are consistent with both CV analyses and DFT calculations.

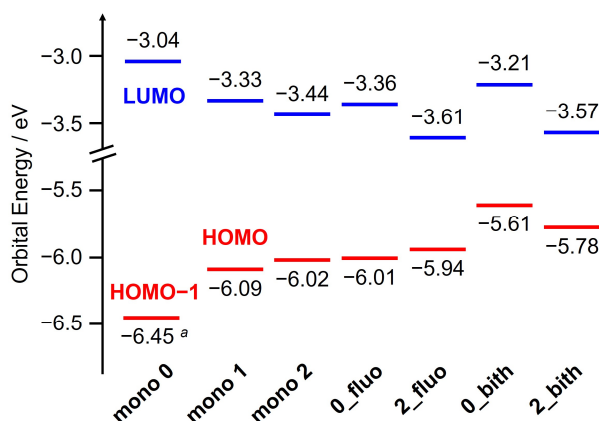


Figure 6. Molecular orbital energy diagram of azobenzene monomer derivatives estimated from cyclic voltammograms and UV–vis absorption bands (π – π^* transition). The data are listed in Table S17.^a The absorption band (π – π^* transition) of **mono 0** is assigned to HOMO–1 $\rightarrow$ LUMO transition in DFT calculation.

We experimentally examined the photophysical properties of azobenzene derivatives. We compared the optical properties of **mono 0**, **mono 1** and **mono 2** (Figure S16). The UV–vis absorption spectra of azobenzene derivatives generally involve two well-separated optical bands.^[5] The large band in the UV region ($\lambda_{\text{abs}} = 310$ nm) and the much weaker band in the visible region ($\lambda_{\text{abs}} = 450$ nm) are attributable to the allowed π – π^* and forbidden n – π^* transitions, respectively. On the other hand, in Figures S16b and S16c, the absorption band of the forbidden n – π^* transition was hardly observed. These spectral features are consistent with 2-hydroxyazobenzene derivatives shown in the previous study by Wyman and coworkers.^[47] The discussion will be given later. Although emission of **mono 2** was detectable (Figure S17), the emission was too weak to precisely determine the absolute photoluminescence (PL) quantum yield. PL spectra of **mono 0** and **mono 1** were not obtained due to low emission properties, similarly to those of

conventional azobenzene derivatives.

Next, we investigated the optical properties of **2_fluo**, **2_bith**, and **2p_fluo**. In Figure S18, we compared UV-vis absorption spectra of **0_fluo** and **2_fluo** (Figure S18a), **0_bith** and **2_bith** (Figure S18b), and **N_fluo** (reported in our previous work^[46]) and **2p_fluo** (Figure S18c). It was commonly clarified that the bathochromic shifts of absorption bands were obtained by the introduction of hydroxy groups. Without hydroxy groups, **0_fluo**, **0_bith** and **N_fluo** hardly exhibited emission, whereas **2_fluo**, **2_bith** and **2p_fluo** showed emission in various solvents. It was revealed that **2_fluo**, **2_bith** and **2p_fluo** should exist at the enol form in the ground state according to the UV-vis absorption data, and emissions originating from ESIPT can be obtained (Figure 7 and Table 1). In non-polar solvents, **2_fluo** exhibited dual emission derived from the enol ($\lambda_{PL} = 640$ nm) and keto ($\lambda_{PL} = 660$ nm) forms (Figure S19 and Table S18). On the other hand, in alcohols, emission from the keto form was significantly suppressed. That is because alcohol molecules act as a hydrogen bond acceptor and inhibit the ESIPT process by the formation of intermolecular hydrogen bonding.^[70] Although similar results obtained from **2_bith**, the results were complicated due to the existence of intramolecular charge transfer (ICT) caused by strong donor characteristics of the bithiophene moieties (Figures S20 and S21, Table S19). In non-protic solvents, the peak tops of PL spectra were bathochromically-shifted as polarity increasing, which is a standard behavior of ICT emission.^[32] In isopropyl alcohol (*i*PrOH) and ethanol (EtOH), on the other hand, the peak tops of PL spectra were hypsochromically-shifted relative to those in dichloromethane (CH₂Cl₂) and chloroform (CHCl₃) even though *i*PrOH and EtOH are more polar than CH₂Cl₂ and CHCl₃. This reversal phenomenon in alcohols should be attributed to suppression of luminescence from the keto form as observed in **2_fluo**. Pang

and coworkers previously investigated in detail a complicated system involving ESIPT and ICT.^[71] According to their report, plausible explanation about luminescent species of **2_bith** can be proposed that three luminescent species might exist (locally excited state (LE), enol form, and keto form) (Figure S21).

In the case of the polymer, **2p_fluo**, although dual emission was observed as with **2_fluo**, unlike **2_fluo**, the PL spectra were hardly affected by the polarity of solvents, and suppression of luminescence from the keto form was not observed in alcohols (Figure S22). Absolute PL quantum yields in various solvents are listed in Table S20, which indicates that the PL properties were improved by expanding the π -conjugation. We investigated the effect of molecular weight on optical properties (Figure S23). As a result, the UV-vis absorption and PL spectra of **2p_fluo** were bathochromically-shifted and the absolute PL quantum yields were improved in all fractions compared to **2_fluo**. However, the absorption and PL wavelengths and absolute PL quantum yield were almost the same in all fractions. These results indicate that π -conjugation is almost saturated in fraction 3 ($M_n = 2,700$, $n = 4$; Table S16).

Furthermore, we examined the PL properties of **2_fluo**, **2_bith** and **2p_fluo** with the spin-coated films. It was revealed that intense emission can be obtained even in the film state, where emission of conventional polymers should be quenched (Figure S24 and Table S21).^[72–74] The absorption and PL wavelengths of **2p_fluo** were bathochromically-shifted and the emission efficiency of **2p_fluo** was improved compared to **2_fluo**. As mentioned above, the π -conjugation of **2p_fluo** was almost saturated in fraction 3, and the optical property of each fraction was almost the same in the film state (Figure S25 and Table S22).

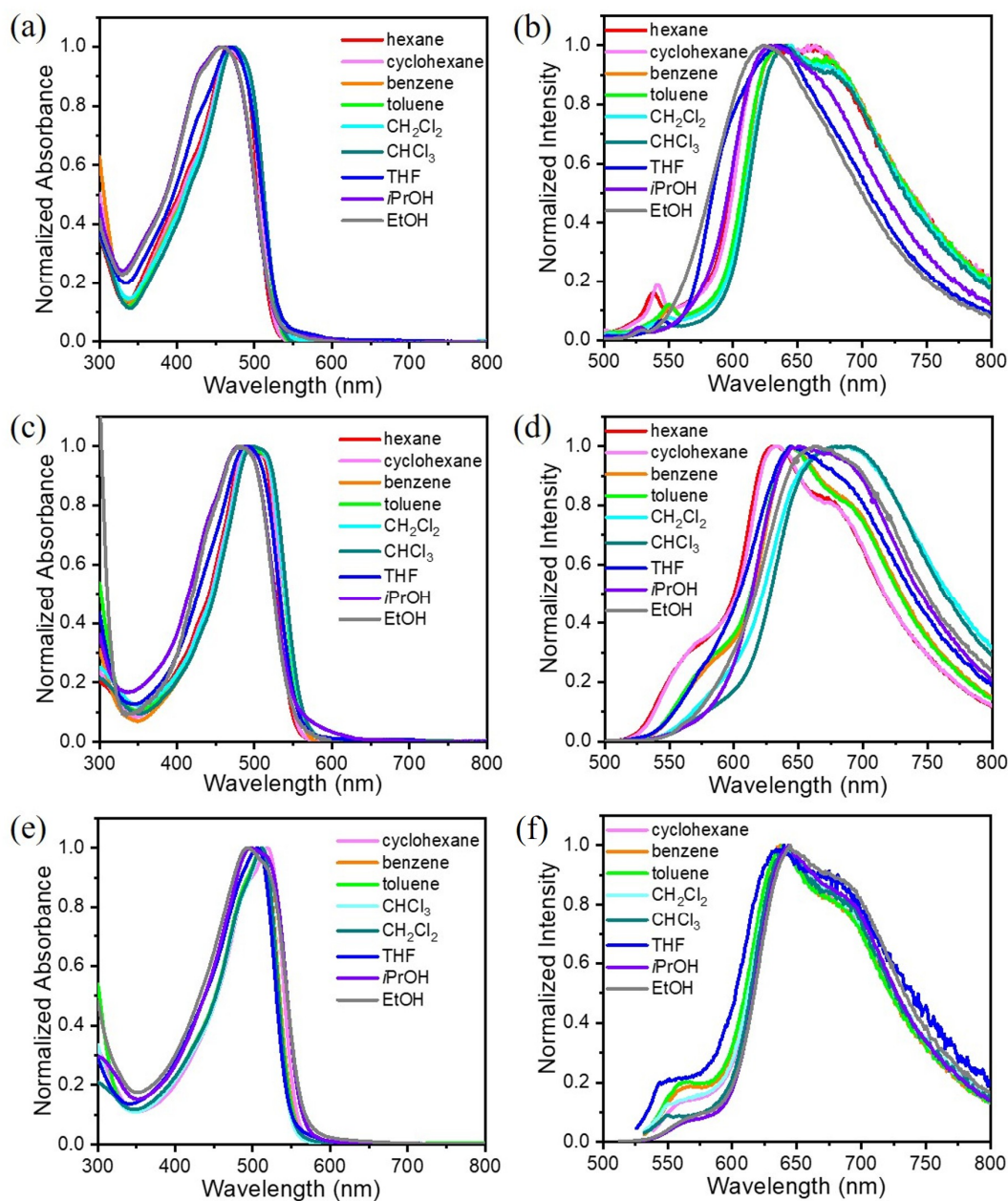


Figure 7. UV-vis absorption and PL spectra of (a,b) **2_fluo**, (c,d) **2_bith**, and (e,f) **2p_fluo** in mixed solvents of CHCl₃/each solvent (1/99, v/v) (1.0×10^{-5} M for monomers, 1.0×10^{-5} M per repeating unit for polymers).

Table 1. Optical data of **2_fluo**, **2_bith**, and **2p_fluo** in various solvents. All data are listed in Tables S18–S20.

Compounds	Solvents	λ_{abs}^a /nm	$\lambda_{\text{PL}}^{a,b}$ /nm	$\Phi_{\text{PL}}^{b,c}$ /%
2_fluo	cyclohexane	468	637, 664	N.D. ^d
	toluene	472	642, 663	N.D. ^d
	CH ₂ Cl ₂	472	645, 662	N.D. ^d
	<i>i</i> PrOH	457	629	N.D. ^d
2_bith	cyclohexane	489	566, 634, 682	0.5
	toluene	495	576, 645, 696	0.6
	CH ₂ Cl ₂	497	683	1.2
	<i>i</i> PrOH	482	645, 692	0.8
2p_fluo	cyclohexane	519	641, 694	1.3
	toluene	512	639, 688	0.6
	CH ₂ Cl ₂	512	643, 688	0.4
	<i>i</i> PrOH	497	644, 695	1.6

^a 1.0×10^{-5} M for **2_fluo** and **2_bith**, and 1.0×10^{-5} M per repeating unit for **2p_fluo** in mixed solvents of CHCl₃/each solvent (1/99, v/v).

^b Excited at λ_{abs} .

^c Absolute PL quantum yield.

^d not detected.

2.4 Acid vapor sensors of polymer films

The performance of polymer films as an acid vapor sensor was evaluated. Although various types of stimuli-responsive luminescent polymers were reported,^[75–79] our polymers exhibited unique stimuli-responsiveness including recording acid exposure history and turn-on luminescent behaviors. We prepared the spin-coated films of **TBS_fluo**, **TBS_bith**, **MOM_fluo**, and **MOM_bith**. Although pristine films of these samples hardly showed emission due to absence of hydrogen bonding, they turned to exhibit emission accompanied by the bathochromic shift in the UV–vis absorption spectra after the deprotection of the protecting groups (TBS and MOM groups) by exposure to

acid vapor (Figures 8, S26, S27, Tables 2, S23–S30, and Movie 1). In particular, **TBS_bith** films which are exposed to TFA vapor show relatively intense emission in the deep-red to NIR region ($\lambda_{\text{PL}} = 692\text{--}709\text{ nm}$, $\Phi_{\text{PL}} = 2.7\text{--}5.9\%$). In addition, they still maintained the real-time detection ability toward acid vapor, which was proposed in our previous study (Movie 2).^[46] In these UV–vis absorption spectra, the measurement under TFA vapor was carried out as illustrated in Figure S28. It is noteworthy that the real-time detection ability of acid vapor, the expression of emission after deprotection, and bathochromic shifts in the UV–vis absorption spectra were similar between TBS and MOM groups. On the other hand, the ease of the deprotection and PL spectra after exposure to TFA vapor were quite different. The deprotection reactions of the TBS groups proceeded faster than those of MOM ones (Figure S29). The reaction progress and presence of byproducts were estimated by ^1H NMR spectra in detail (Figures S30–S37). To simplify the analysis, we used compounds **9**, **12**, **14**, and **15** as model compounds. As a result, deprotecting reactions mostly proceeded in both TBS and MOM groups. In the case of TBS groups, *tert*-butyldimethylsilanol only emerged as a byproduct after deprotection. On the other hand, in the case of MOM groups, neither starting material nor product signals were observed in downfield ($\delta = 7\text{--}8\text{ ppm}$).

To evaluate the performance of TBS groups in detail, we compared **TBS_fluo** and **2p_fluo** films after exposure to TFA vapor (Figure S38). UV–vis absorption spectra after exposure to TFA vapor and PL spectra were different each other. The difference might be derived from incompleteness of deprotection or existence of byproduct. To gather information, we performed additional optical measurements. In Figure S39, we measured UV–vis absorption and PL spectra of the films prepared by adding *tert*-butyldimethylsilanol to **2_fluo**, **2_bith**, and **2p_fluo**. It was shown that the spectra were

corresponded regardless of the amount of *tert*-butyldimethylsilanol added. Therefore, it is suggested that the difference between **TBS_fluo** film after exposure to TFA vapor and **2p_fluo** film should be derived mainly from incompleteness of deprotection. However, there was little effect on the performance of the acid vapor sensor film. The UV-vis absorption spectra under TFA vapor are consistent with each other.

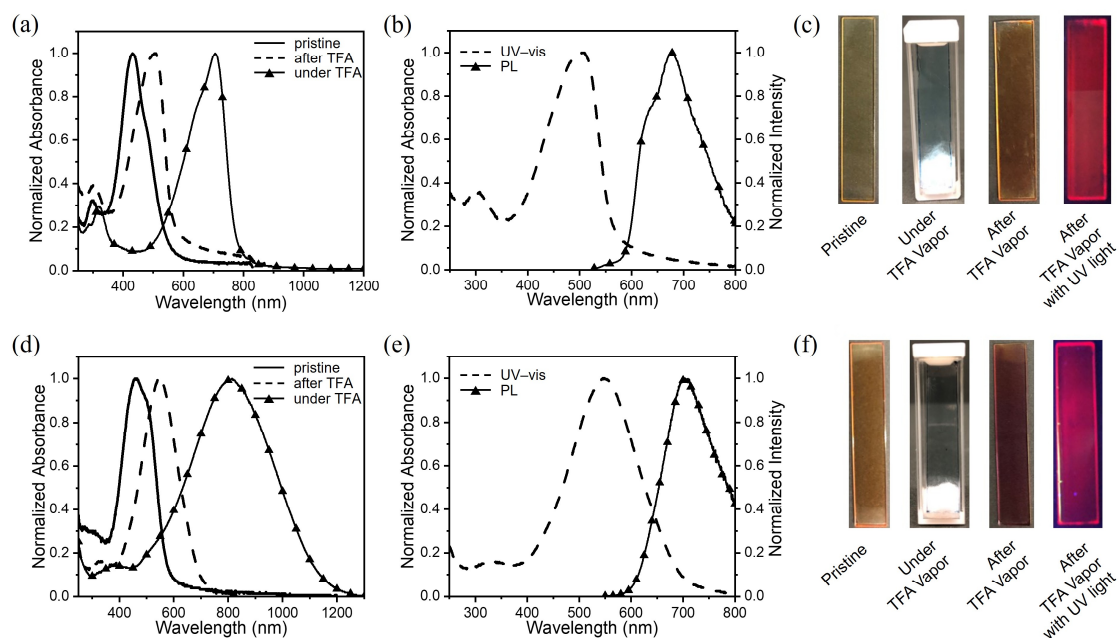


Figure 8. (a,d) UV-vis absorption and (b,e) PL spectra, and (c,f) photographs in film state of **TBS_fluo** (a,b,c, $M_n = 21,000$, $M_w = 29,000$,) and **TBS_bith** (d,e,f, $M_n = 28,000$, $M_w = 42,000$). In PL spectra, the films are exposed to TFA vapor until the spectra are no longer changed. These film samples were prepared via the spin-coating (1000 rpm, 30 seconds) on the quartz substrate (0.9 cm $\times$ 5 cm) with CHCl_3 solutions (0.15 mL, concentration: 1 mg / 300 μL , 1000 rpm, 30 sec). In UV-vis absorption spectra, “pristine” shows pristine films after spin-coating, “after TFA” shows films after exposure to TFA vapor until the spectra are no longer changed, and “under TFA” shows exposing TFA vapor like shown in Figure S28. The photographs are taken under room light and UV (365 nm) irradiation.

Table 2. Optical data of deprotected polymer films ^a

Polymers ^b	$\lambda_{\text{abs, pris}}^c$ /nm	$\lambda_{\text{abs, after}}^c$ /nm	$\lambda_{\text{abs, under}}^c$ /nm	λ_{abs}^c /nm	λ_{PL}^d /nm	Φ_{PL}^e /%
TBS_fluo	431	508	705	508	676	1.0
TBS_bith	460	546	815	546	702	5.9
MOM_fluo	442	504	709	504	684	3.0
MOM_bith	470	544	818	544	692	1.3

^a Prepared via the spin-coating (1000 rpm, 30 seconds) on the quartz substrate (0.9 cm × 5 cm) with CHCl₃ solutions (0.15 mL, concentration: 1 mg / 300 μ L).

^b fraction 2; M_n = 21,000, M_w = 29,000 for **TBS_fluo**, M_n = 28,000, M_w = 42,000 for **TBS_bith**, M_n = 30,000, M_w = 48,000 for **MOM_fluo**, M_n = 38,000, M_w = 64,000 for **MOM_bith**.

^c λ_{abs} : the maximum absorption wavelength. $\lambda_{\text{abs, pris}}$: λ_{abs} of the pristine film. $\lambda_{\text{abs, after}}$: λ_{abs} of the film after exposure to TFA vapor until the spectra are no longer changed. $\lambda_{\text{abs, under}}$: λ_{abs} of the film exposure to TFA vapor.

^d Excited at λ_{abs} .

^e Absolute PL quantum yield excited at λ_{abs} .

2.5 Thermostability of the polymers

Finally, we performed thermogravimetric analysis (TGA) to investigate thermal stability of the polymers. We determined degradation temperatures with 5 wt% weight losses (T_{d5}) with the synthesized polymers and model compounds having the similar structure (**N_fluo**) (Figure S18).^[46] Accordingly, all polymers showed degradation temperatures in the higher temperature region ($T_{d5} > 300$ °C). It is likely that robust conjugation systems through polymer chains could be responsible for thermal stability. However, it was observed that the synthesized polymers were less thermally-stable than the model compounds (Figure S40, Tables S31 and S32). This might be caused by the substitutions at *ortho* position. In the cases of **TBS_fluo** and **TBS_bith**, **MOM_fluo** and **MOM_bith**, there were partial weight losses below decomposition of the polymer main chain, indicating that protecting groups were decomposed before main-chain

decomposition. From **2p_fluo**, decomposition occurred earlier than **N_fluo**, and it is due to hydroxy substitution. This decrease in thermal stability is similarly observed in other types of polymers with hydroxy substitutions and considered to be due to the intermolecular dehydration reaction at the phenolic hydroxy moiety.^[80]

3. Conclusion

To verify the expression of the luminescence properties based on theoretical calculations, we designed and synthesized o-hydroxylated azobenzene derivatives. Through the rational molecular design with the formation of hydrogen bonds and the expansion of π -conjugation, the compounds showed ESIPT emission via the stabilization of n-orbitals with the suppression of photoisomerization and the allowance of S_0 – S_1 transition. As a result, the synthesized polymers exhibited relatively intense emission ($\lambda_{PL} = 702$ nm, $\Phi_{PL,max} = 5.9\%$) among azobenzene derivatives without metal complexation. In addition, to demonstrate the usefulness of the azobenzene polymers as a functional luminescent material, we applied the polymers for a film-type acid vapor sensor. The sensors demonstrated real-time detection ability toward acid vapor triggered by the protonation at the nitrogen atoms. Furthermore, it is also possible to discriminate whether this film sensor has been used for acid sensing in the past according to the progress of deprotection of the TBS protecting group. This study theoretically and practically demonstrated that azobenzene-based polymers are a promising platform for constructing luminescent π -conjugated materials.

Acknowledgement

This work was partially supported by Japan Society for the Promotion of Science (JSPS), a Grant-in-Aid for Scientific Research (B) (JP23K23398) (for M.G.) and (JP24K01570) (for K.T.).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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