

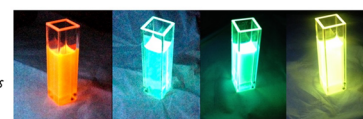
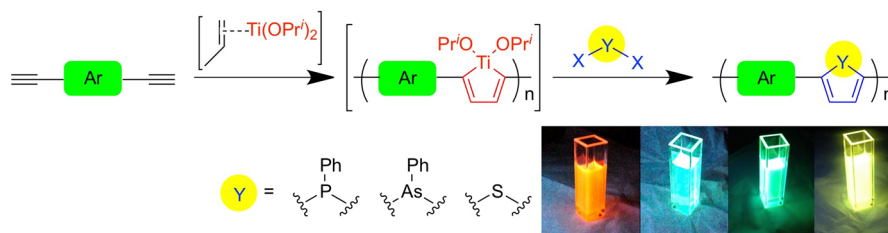
Application Note

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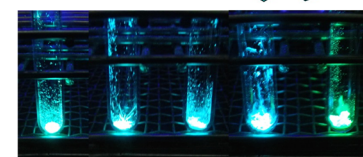
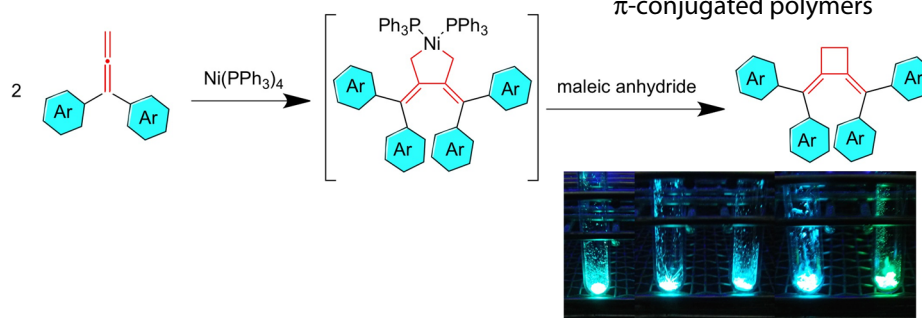
Synthesis and Evaluation of Various Photoluminescent Materials via New Organometallic Chemistry Routes

– Utilization of Ultraviolet-visible (UV-vis) Absorption and Photoluminescence (PL) Spectra –

Yoshimasa Matsumura ⁽¹⁾, Hiroshi Eguchi ⁽²⁾, Ikuyoshi Tomita ⁽²⁾



Heteroatom-containing π -conjugated polymers



High efficiency aggregation-induced emission dyes

Electric and Electronic Industry

1. Introduction

Organic molecules and macromolecules with extended conjugated π -electron systems exhibit intriguing electronic and optical properties, and they are expected to serve as next-generation functional materials for organic film solar cells, organic transistors, organic electro-luminescence (OEL) devices, etc. In particular, the materials utilizing the photoluminescent properties are applicable not only to OEL but also many fields, such as chemical sensors, PL imaging probes, etc. Since the photoluminescence properties, i.e. colors and intensities, depend on the chemical structure of the materials, synthetic methods that enable versatile molecular designs of this class of materials are significantly important. This article introduces synthetic methods for "heteroatom-containing unprecedented π -conjugated polymers" and "high efficiency aggregation-induced emission (AIE) dyes" we reported recently, as well as the successful results obtained by the evaluation of their optical features using an UV-vis spectrophotometer (UV-3100) and spectrofluorophotometers (RF-5300 or RF-6000).



Fig. 1 Shimadzu spectrofluorophotometer, RF-6000, used for fluorescence measurements

2. Group 15 elements-containing π -conjugated polymers ^{[1], [2]}

Among a number of π -conjugated polymers reported to date, those containing heterocyclic structures such as heteroles are attractive functional materials that often exhibit excellent fluorescence properties. Since

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energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the heterole units are affected largely by the incorporated heteroatoms, it is expected that the color of their photoluminescence can be tuned by varying both the heteroatoms and the repeating structures of the π -conjugated polymers.

In most cases, the heterole-containing polymers are obtainable by the transition metal-catalyzed polycondensation of monomers carrying the corresponding heteroles. However, some heteroles are not stable enough as monomers or may inhibit the polymerizations. Accordingly the synthesis of π -conjugated polymers with such heterole units has scarcely been investigated.

The heteroles containing the group 15 elements such as phospholes exhibit unique electron-accepting property based on the $\sigma^*-\pi^*$ orbital interaction.^[3] Although they are expected to serve as building blocks for functional materials, only several reports have described the synthesis of phosphole-containing polymers.^{[4]-[6]} Concerning the arsole-containing polymers, within the knowledge of the authors, no report has described their synthesis, although the arsoles may exhibit much excellent oxidation-resistant properties which are attractive for many applications.

To establish synthetic methods of a variety of heterole-containing polymers, we have been working

on the synthesis and reactions of organometallic polymers possessing reactive carbon-metal bonds in the main chain. In particular, it was found that π -conjugated polymers possessing heteroles in the main chain can be obtained by the reactions of organometallic polymers, which are generated by the polymerization based on the regioselective metallacyclization between terminal acetylenes and a low-valent titanium complex,^[7,8] with various electrophiles containing heteroatoms (Fig. 2).^[9-12] On the basis of the transformations of the organotitanium polymers, π -conjugated polymers containing phosphole and arsole, could be achieved.

As a typical example, the titanacyclopentadiene-containing polymer (**3a**) was prepared by the reaction of a diene monomer (**1a**) with a titanium complex (**2**) from -78°C to -50°C in diethyl ether (Fig. 3). This polymer (**3a**) was subjected to the transformation into a phosphole-containing polymer (**4a-P**) and an arsole-containing polymer (**4a-As**) by reactions with dichlorophenylphosphine and diiodophenylarsine, respectively. The obtained polymers containing group 15 elements are dark red colored materials that exhibit orange photoluminescence upon the irradiation with ultraviolet light.

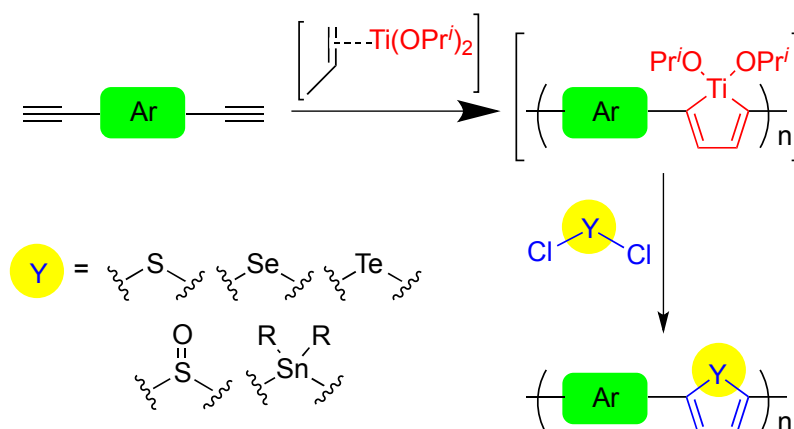


Fig. 2 Synthesis of π -conjugated polymers containing various heteroles via organotitanium polymers

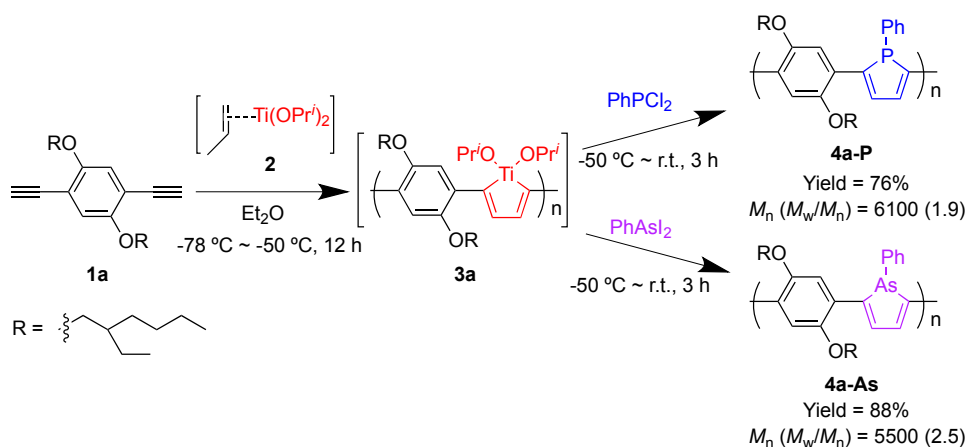


Fig. 3 Synthesis of phosphole- and arsole-containing polymers via an organotitanium polymer

The optical characteristics of the obtained polymers are evaluated from the UV-vis absorption spectra and PL spectra (Fig. 4, Table 1). For example, in the UV-vis absorption spectrum of **4a-P**, the absorption maximum (λ_{max}) and absorption onset (λ_{onset}) are 522 nm and 620 nm, respectively. These values are more than 100 nm longer than those of a diarylphosphole derivative (**P-model**)^[1], which was synthesized as a model compound. This result suggests that the π -conjugation takes place effectively along the polymer main chain. Compared to the case of a thiophene-containing polymer^[12] ($\lambda_{\text{max}} = 407$ nm, $\lambda_{\text{onset}} = 520$ nm), which was likewise synthesized via the organotitanium polymer, the phosphole-containing polymer proved to exhibit its absorption in a longer wavelength range by approximately 100 nm. These results suggest that the band gap of the phosphole-containing polymer is narrower reflecting on the lower LUMO energy level

due to the $\sigma^*-\pi^*$ orbital interaction as expected for the heavier group 15 elements-containing heteroles. Likewise, the absorption spectrum of the arsole-containing polymer (**4a-As**) appeared in the longer wavelength region compared to that of the model compound (**As-model**)^[13]. It is also plausible that the arsole skeleton exhibits a low LUMO energy level due to the $\sigma^*-\pi^*$ orbital interaction.

The PL spectra of the polymers were measured on the RF-5300 spectrofluorophotometer under the excitation light at their λ_{max} . The emission maxima (E_{max}) of **4a-P** and **4a-As** were 593 nm and 600 nm and fluorescence quantum yields (Φ) were 0.10 and 0.05, respectively. Thus, **4a-P** and **4a-As** were found to exhibit spectral similarities, while their electrochemical redox properties were dramatically different stemming from nature of the elements.^[2]

Table 1 Optical properties of phosphole- and arsole-containing π -conjugated polymers and their model compounds

Compounds	λ_{max} ^{a)} (nm)	λ_{onset} ^{a)} (nm)	E_{max} ^{b)} (nm)	Φ ^{c)}	$E_{\text{g(opt)}}$ ^{d)} (eV)
P-model ^[1]	396	448	477	0.57	2.77
4a-P	522	620	594	0.10	2.00
As-model ^[13]	395	446	476	0.51	2.78
4a-As	517	612	600	0.05	2.02

a) Measured in CHCl_3 ; b) Emission maxima, irradiated at their λ_{max} (nm); c) The quantum yields (Φ) were estimated at ambient temperature using quinine sulfate in 0.50 M sulfuric acid aqueous solution as a standard; d) Estimated from λ_{onset} .

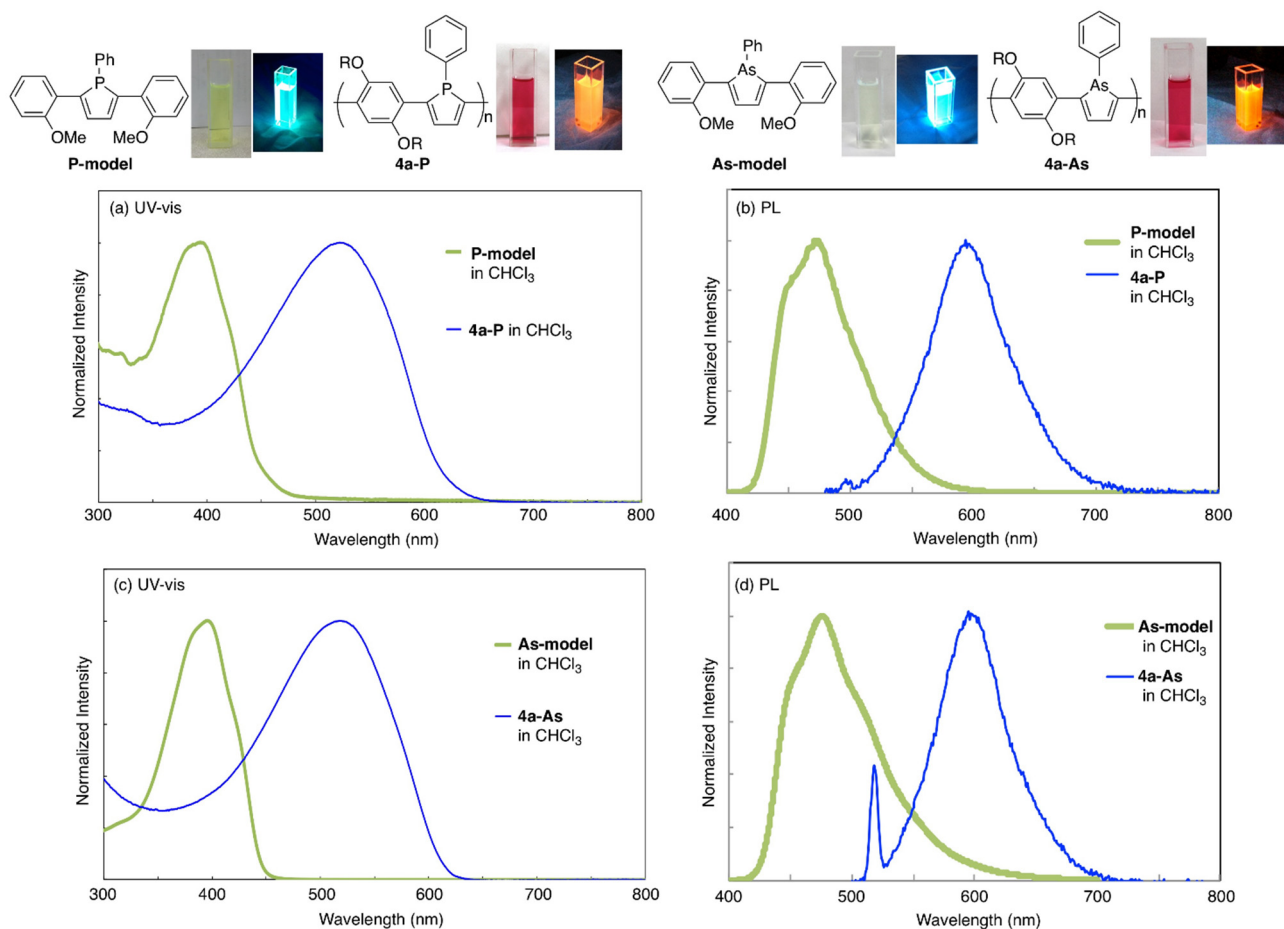


Fig. 4 (a, c) UV-vis absorption spectra and (b, d) PL spectra

3. Parallel synthesis of photoluminescent polymers via an organotitanium polymer^[14]

As described above, polymers having diverse structures are now accessible by the polymer reactions associated with the main chain-transformation of the organotitanium polymers. Using this method, various functional materials having different properties can be derived in a parallel way starting from a single organotitanium reactive polymer. With an objective to obtain polymers with excellent photoluminescence, three kinds of polymers were prepared by the reactions of a fluorene-containing organotitanium polymer (**3b**) (Fig. 5). That is, **3b** was prepared from a 2,6-diethynylfluorene derivative (**1b**) and the titanium complex (**2**) which was then transformed to thiophene, butadiene, and phosphole-containing polymers (**4b-S**, **4b-H**, and **4b-P**) by reactions with sulfur monochloride,

hydrochloric acid, and dichlorophenylphosphine, respectively.

The UV-vis absorption spectra of **4b-S**, **4b-H**, and **4b-P** were measured from which their λ_{\max} were observed at 407 nm, 438 nm, and 478 nm, respectively (Fig. 6, Table 2). The longer wavelength absorption observed in **4b-P** is in good accordance with the lower LUMO energy level of the phosphole unit leading to the narrower band gap as mentioned above.

These polymers exhibit excellent photoluminescent properties, whose color depends on the building blocks in the polymers: **4b-S** in blue, **4b-H** in green, and **4b-P** in yellow. The PL spectra, measured on the RF-5300, supported further that these polymers emit light in different wavelengths with good efficiency (Fig. 6).

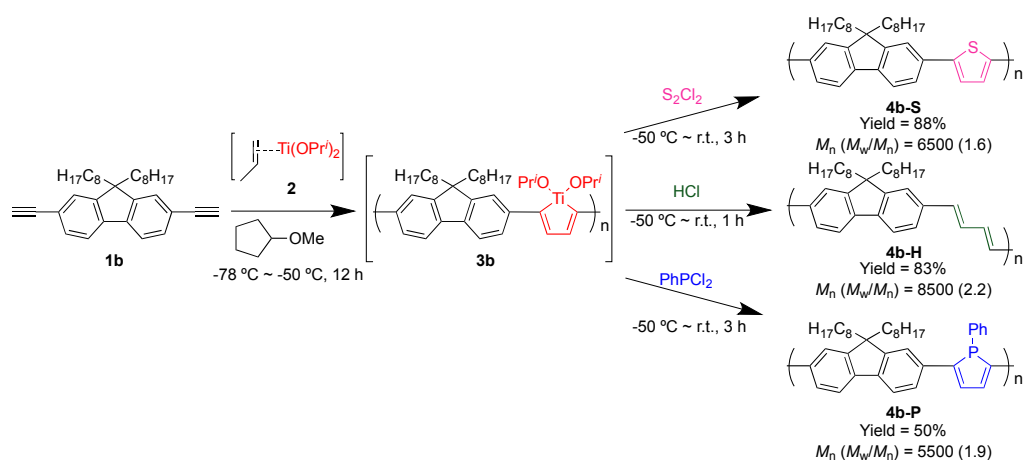


Fig. 5 Parallel synthesis of photoluminescent polymers by the reaction of a fluorene-containing organotitanium polymer

Table 2 Optical properties of polymers

Polymers	λ_{\max}^a (nm)	λ_{onset}^a (nm)	E_{\max}^b (nm)	Φ^c	$E_{g(\text{opt})}^d$ (eV)
4b-S	407	483	470	0.18	2.56
4b-H	438	499	485	0.30	2.48
4b-P	478	546	529	0.37	2.27

a) Measured in CHCl_3 ; b) Emission maxima, irradiated at their λ_{\max} (nm); c) The quantum yields (Φ) were estimated at ambient temperature using quinine sulfate in 0.50 M sulfuric acid aqueous solution as a standard; d) Estimated from λ_{onset} .

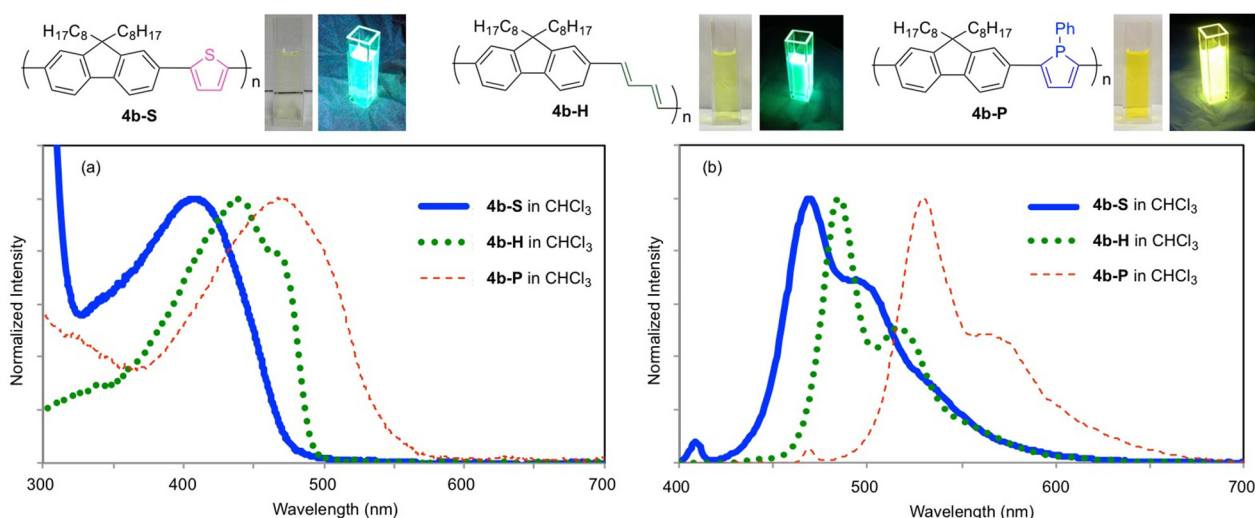


Fig. 6 (a) UV-vis absorption spectra and (b) PL spectra

As a model compound for explosives consisting of nitrated aromatic moieties, nitrobenzene was added to a solution of the phosphole-containing polymer (**4b-P**), by which a remarkable fluorescence quenching was observed. The same quenching phenomenon was also observed with the polymer in the solid state. These results may suggest that this polymer can be applied to a turn-off type PL chemosensor (Fig. 7).

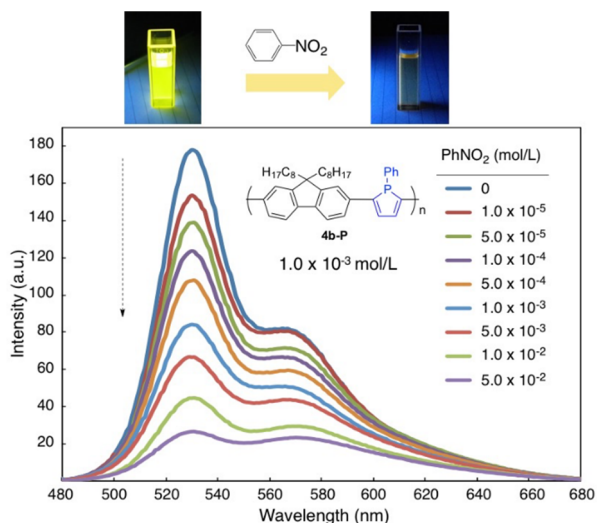


Fig. 7 Quenching phenomenon of **4b-P** by addition of nitrobenzene (in CHCl_3)

4. Synthesis of AIE dyes by cyclodimerization of allenes using a nickel complex^[15]

Many photoluminescence-active π -conjugated compounds emit light only in diluted solutions. At high concentration in solutions or in the solid state, the photoluminescence efficiency becomes very low due to the concentration quenching. On the other hand, photoluminescent molecules that do not undertake concentration quenching are attractive in many applications such as light emitting devices, because they

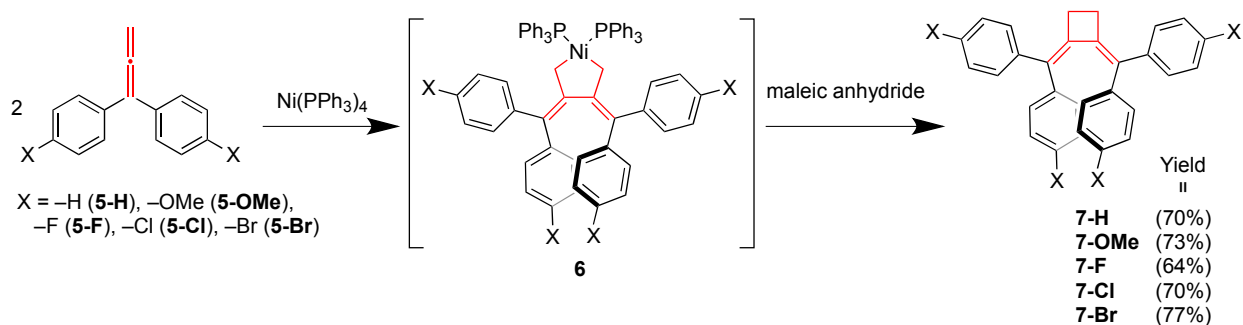


Fig. 8 Cyclodimerization of 1,1-diaryllenes

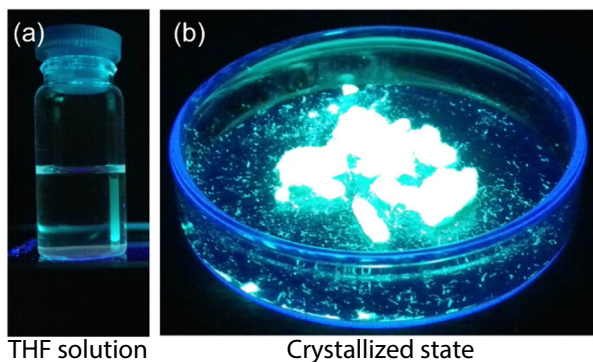


Fig. 9 Photoluminescent behavior of a cyclodimer (**7-H**)

are commonly employed in the solid state. Among the solid state photoluminescent materials, those exhibiting aggregation-induced emission (AIE) properties, in which the photoluminescence efficiency switches from low in solution to high in the solid state,^[16-19] are attracting attentions for advanced applications such as fluorescent chemosensors. At present, only several highly substituted unsaturated compounds, such as tetraphenylethene, are known to serve as AIE manifesting molecules. Accordingly, the development of novel AIE dyes with high fluorescence quantum yields is a significant research subject.

Although cisoid 1,1,4-tetraaryl-1,3-butadiene derivatives are thermodynamically unfavorable, they are known to have a twisted π -electronic systems that prevent from intermolecular π - π stacking and may provide a chance for good solid state photoluminescence properties. As a new class of AIE molecules, we focused on a 1,2-dimethylenecyclobutane skeleton,^[20-23] in which a cyclobutane ring is fused to the butadiene at the 2- and 3-positions. The 1,2-dimethylenecyclobutane derivatives are expected to have conformationally fixed cisoid 1,3-butadiene units and the twisted π -conjugated system if substituents on the two methylenes are adequately designed, by which unique AIE dyes would be developed. We found that the cyclodimerization of 1,1-diaryllenes (**5**) takes place effectively to produce cyclodimers (**7-H**, **7-OMe**, **7-F**, **7-Cl**, and **7-Br**) by using a nickel complex, followed by the treatment with maleic anhydride (Fig. 8).

In the UV-vis absorption spectra of the obtained cyclodimers measured in a tetrahydrofuran (THF) solution, the absorption attributed to the π - π^* transition was observed in the range of $\lambda_{\text{max}} = 352 \text{ nm}$ to 373 nm . Concerning the photoluminescent behaviour of the cyclodimers, it was found that they exhibit clear AIE properties whose luminescence intensities are influenced largely by the measurement conditions. For example, **7-H** exhibits almost no light emission in a THF solution (Fig. 9-a), while a strong green emission was

observed in the solid state (Fig. 9-b). The AIE behaviors were likewise observed in all the synthesized cyclodimers. When the PL spectra of the cyclodimers were measured in the solid state on the RF-6000 instrument equipped with an integral sphere, E_{max} was observed in the range of 476 nm to 509 nm whose fluorescence quantum yield reached to $\Phi = 0.85$ (7-Br), indicating that the cyclodimers serve as extremely

high efficiency photoluminescent dye in the solid state (Fig. 10, Table 3). On the basis of the nickel-mediated cyclodimerization, various cyclodimers with different substituents will be designed by the facile structural design of the allenes. These AIE dyes that exhibit a highly efficient photoluminescence in the solid state will be attractive for many applications.

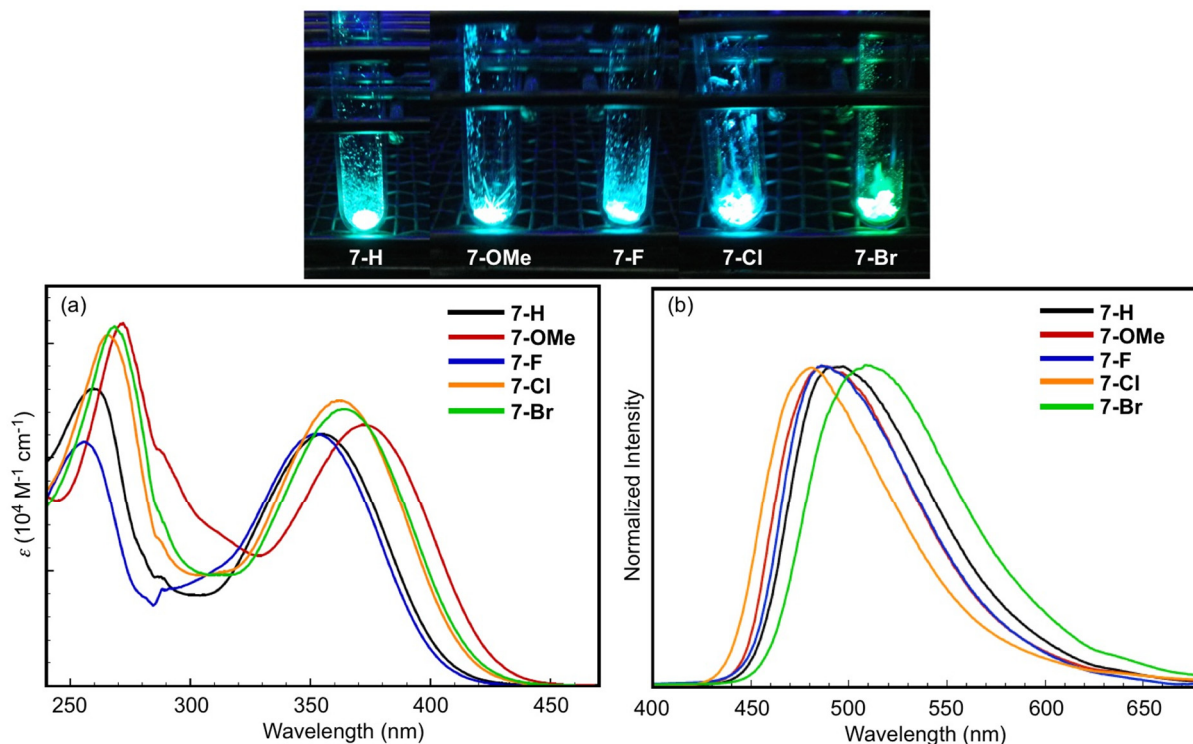


Fig. 10 (a) UV-vis absorption spectra of cyclodimers taken in THF solutions and (b) their PL spectra in the solid state

Table 3 Optical properties of cyclodimers

Compounds	$\lambda_{\text{max}}^{\text{a}}$ (nm)	$\lambda_{\text{onset}}^{\text{a}}$ (nm)	ϵ^{a} ($10^4 \text{ M}^{-1} \text{ cm}^{-1}$)	$E_{\text{g(opt)}}^{\text{b}}$ (eV)	$E_{\text{max}}^{\text{c}}$ (nm)	Φ^{d}
7H	260, 354	405	2.60, 2.20	3.06	493	0.80
7-OMe	272, 373	425	3.18, 2.28	2.92	487	0.54
7-F	256, 362	403	2.14, 2.21	3.08	486	0.33
7-Cl	266, 362	415	3.07, 2.50	2.99	481	0.71
7-Br	269, 365	418	3.15, 2.43	2.97	509	0.85

a) Measured in THF ($4 \times 10^{-5} \text{ M}$); b) Optical HOMO-LUMO gap, estimated from $\lambda_{\text{onset}}^{\text{c}}$; c) Measured in the solid state, irradiate at 350 nm; d) Determined using the integrating sphere method.

5. Summary

Photoluminescent π -conjugated polymers and AIE dyes were newly prepared by the novel synthetic routes utilizing organometallic chemistry. Their unique optical properties were evaluated by the UV-vis spectrophotometer (UV-3100) and the spectrofluorophotometers (RF-5300 or RF-6000). By exploiting new synthetic methods, we could obtain unprecedented materials that are potentially attractive for optical applications. Further studies on the new synthesis and applications of the produced functional materials are on going.

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First Edition: Apr. 2018



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