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Highlight Review

Luminescent Organoboron Conjugated Polymers

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Abstract

The incorporation of luminescent organoboron dyes into π-conjugated polymer backbones is attractive for potential applications as electroluminescent devices, organic field-effect transistors, and photovoltaics. Recent advances in the field of organoboron polymers are reviewed here.

◆ Introduction

Because of academic interest and potential applications as flat panel displays,[1] much effort has been devoted to the design and synthesis of various conjugated polymers. Extensive research has been performed to develop highly efficient light-emitting polymers with tunable emission, long lifetimes, and color purity.[2] Presently, conjugated polymers are used for a multiplicity of optoelectronic applications such as light-emitting diodes,[3] photovoltaic devices,[4] and field-effect transistors.[5] A wide range of polymers, such as poly(*p*-phenylenevinylene) (PPV), polythiophene (PT), poly(*p*-phenylene) (PPP), poly(phenylene–ethynylene) (PPE), polyfluorene (PF), and their derivatives, have been extensively investigated as emissive materials.[6–10] However, the simple backbones of such conjugated polymers lead to limitation of the π-conjugated system, e.g., high emission efficiency, fine-tunability of their band gap, processibility, dramatic improvements in the durability and stability of the polymers. Therefore, it is necessary to explore further new π-conjugated systems.

Recently, boron-containing π-conjugated systems have attracted much attention due to their intriguing properties such as low-lying LUMO orbitals, ease of reduction, and a bathochromic shift of the absorption and emission spectra, resulting from the conjugative overlap of the π orbital via the vacant p orbital of the boron atom.[11] Previously, we have developed various organoboron π-conjugated polymers,[11] especially poly(*p*-phenylenevinylene–borane)[12] and poly(*p*-phenylene–borane),[13] exhibiting high luminescence with large Stokes shifts as a new class of n-type semiconductors[14] (Figure 1). Depending on the nature of the arenediyl bridge, these polymers act efficiently as chemosensors for anions and toxic small molecules.[15] On the contrary, vacant p-orbital tricoordinate boron complexes between neighboring π-conjugated subunits lack chemical stability due to the high Lewis acidity of boron.

Therefore, in this highlight review we focus on luminescent organoboron dyes,[16] boron quinolate,[17] boron diketonate,[18] boron dipyrromethene (BODIPY),[19] pyrazabole,[20] etc, consisting of more stably tetracoordinate boron architecture in order to possess impressive optical properties such as high luminescent quantum yields, large extinction coefficients, and two-photon absorption cross section (Figure 2). Our synthetic design is the incorporation of such organoboron dyes into the polymeric conjugated scaffold. Their designed polymers lead to unique properties such as strong fluorescence and efficient energy migration to boron-chelating moieties by extending π conjugation along the polymer backbone. Herein, we describe our recent development of organoboron polymers that incorporate various organoboron dyes into a polymeric π-conjugated system. Finally, unique π-conjugated polymers based on carboranes as icosahedral boron clusters are also introduced.

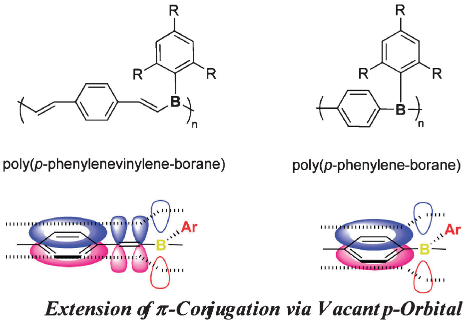

Figure 1. Chemical structures and π-conjugated system of poly(*p*-phenylenevinylene–borane) and poly(*p*-phenylene–borane).

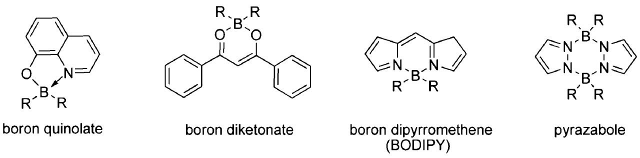

Figure 2. Molecular structures of organoboron dyes.

◆ Boron Quinolate

Organoboron quinolate is an important candidate for luminescent device materials possessing potentially useful properties as electron conduction and emissive components in organic light-emitting devices (OLEDs).[17a,17b] The fusion of these compounds and polymeric materials is expected to be advantageous due to improved processsability such as film-formability, thermal- and photo stability. Therefore, the poly-

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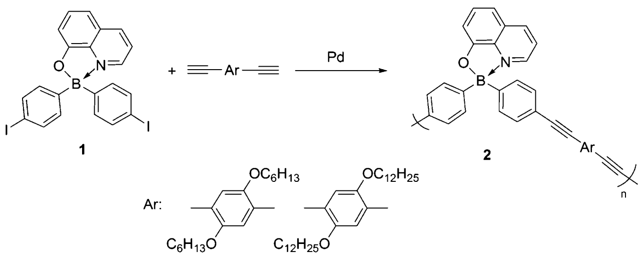


Scheme 1. Synthesis of boron quinolate conjugated polymers.

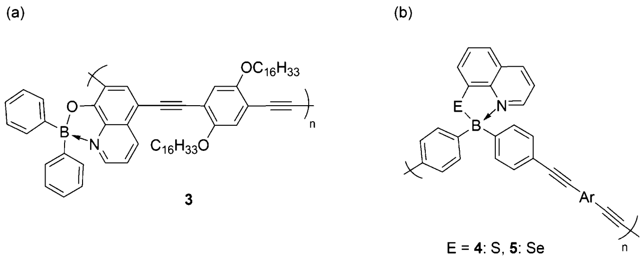


Figure 3. Molecular structures of (a) organoboron quinolate polymer linked on 5,7-position of quinolate moieties and (b) organoboron quinoline-8-thiolate and quinoline-8-selenolate polymers.

meric boron quinolate was first reported by Jäkle et al. Well-defined polymers incorporating boron quinolates into a polystyrene side chain were efficiently prepared via multistage polymeric reaction of poly(4-dibromoborylstyrene).[21] Continuously, Weck et al. also proposed the potentiality of organoboron quinolate-functionalized polystyrene as excellent precursors for OLETs.[22]

We have recently prepared novel boron quinolate polymers with π-conjugated backbones (Scheme 1).[23] *p*-Diiodobenzene-functionalized boron quinolate monomer **1** was polymerized by organometallic polycondensation (Sonogashira coupling) to produce the conjugated polymers **2** incorporating organoboron quinolate into the main chain. No bathochromic shifts of absorption and fluorescence maxima of the polymers were observed as compared with **1**, because different *p*-phenylene–ethynylene units in the polymers were attached to sp^3-hybridized boron atoms. However, the polymers emit intense blue-green light with good quantum yields under a wide range of excitation wavelengths and exhibit efficient energy migration. Emission color of the polymers was freely tuned by substituting methyl groups into the quinolate ligands.[24] Further, incorporation of more stable organoboron aminoquinolate of similar structure to boron quinolate into π-conjugated polymers led to higher molar absorption coefficients while retaining good quantum yields.[25] To improve further the π-conjugated system of boron quinolate polymers, we have also reported synthesis of a main-chain organoboron quinolate polymer **3** linked at the 5,7-positions of quinolate moieties (Figure 3).[26] The polymers were prepared via polymeric reaction of 8-hydroxyquinoline poly(*p*-phenylene–ethylene) and showed high molar extinction coefficient whose value was eight times higher than nonsubstituted boron quinolate. Much bathochromic shift of the polymer was observed in comparison with the polymer precursor. More recently, novel organoboron quinoline-8-thiolate and quinoline-8-selenolate polymers **4** and **5** were also prepared by the Sonogashira coupling of diiodobenzene-functionalized boron quinoline-8-thiolate and -selenolate monomers.[27] Accordingly, increasing atomic number of the 16 group atom adjacent to the boron atom caused emission shift to longer wavelength and decreasing of the quantum yields for both model compounds and the polymers. However, the polymers showed high refractive indices ($n_d > 1.66$).

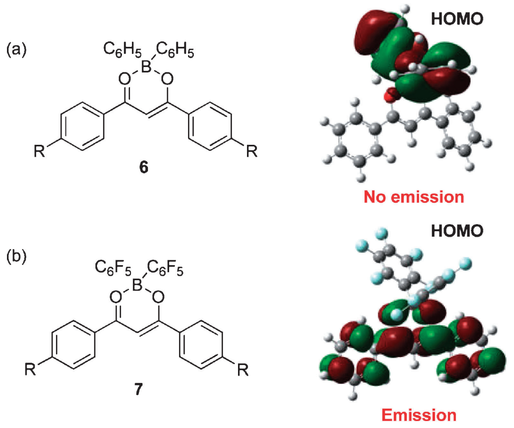
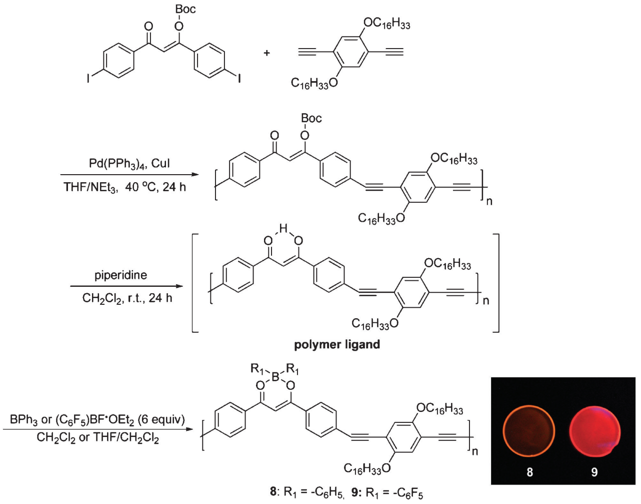


Figure 4. Molecular structures and molecular orbital diagrams for the HOMO (B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p)) of **6** (a) and **7** (b).

Boron Diketonate

Organoboron diketoinate is also a boron light-emitting material exhibiting large molar absorption coefficients and high quantum yields.[18] Conjugation of boron diketonate arises due to inhibition of nonradiative dissipation through O–H stretching modes from tautomerization between ketone and enol structures by forming stable six-membered boron-chelating rings, and the boron complex shows no loss of the unique characteristics of the diketonate fluorophore such as high fluorescence quantum yield, and high photostability, in contrast to heavy-metal complex. Fraser et al. have recently studied the preparation of difluoroboron dibenzoylmethane (difluoroboron diketonate)-end-functionalized polylactides (BF_2dbmPLA),[28] poly(ε-caprolactone),[29] and their block copolymers[30] exhibiting interesting phosphorescence by ring-opening polymerization of lactides or ε-caprolactone using boron diketonate with a hydroxy group as an initiator. Further, low-molecular weight BF_2dbmPLA film with weak emission and strong phosphorescence act as sensors for aerodynamics applications.[31] However, the presence of B–F bonds in the difluoroboron diketonate results in some instability under irradiation and sensitivity to polar solvents. To overcome these disadvantages, we proposed the synthesis of novel diarylboron diketonates possessing larger molar absorption coefficients and high quantum yields.[32] Their emission behaviors depend on the electronic structures of boron atoms; that is, although boron complex **7** bearing strong electron-withdrawing C_6F_5 groups showed high fluorescence, no emission of **6** with diphenyl groups was observed because the highest occupied molecular orbital (HOMO) of **6** is not localized on the diketonate moiety (Figure 4). Herein, we anticipated that the emission of diphenyl diketonate moiety is restored by extending



Scheme 2. Synthetic route of organoboron 1,3-diketonate polymers **8** and **9** and the inset shows photographs of **8** and **9** in the film states under UV irradiation (365 nm).

π conjugation along the polymer linker; i.e., the HOMO of diphenylboron moiety is delocalized on the whole of the polymeric diketone ligand. Thereafter, the first main chain organoboron 1,3-diketonate polymers were prepared by highly efficient chelating reaction of 1,3-diketone *p*-phenylene–ethynylene derivative as a polymeric ligand with the appropriate organoboron reagents (Scheme 2).[33] The polymers showed significantly red-shifted absorption and fluorescence emission maxima relative to a polymeric ligand, and the emission maxima in film states were dramatically red-shifted to longer wavelength region compared with those in solution states. The polymers with diphenyl **8** and pentafluorodiphenyl **9** groups attached on the boron emit orange and red light, respectively, which were excited at respective absorption maxima attributable to *p*-phenylene–ethynylene moiety, as a result of extended π conjugation along the polymeric ligand.

Boron Dipyrromethene

Boron dipyrromethenes (BODIPYs) and their derivatives are an important class of highly luminescent materials that have found widespread applications in fluorescent dyes for biochemical labeling, photonic molecular systems, laser dyes, organogelators, and light-emitting devices[19,34] due to high quantum yields, low rates of intersystem crossing, large molar absorption coefficients, and excellent photostability. Recently, the incorporation of the BODIPYs as electroluminescent chromophores into polymer side chains[35] and silica matrices[36] is attractive for optoelectronic applications as dye laser. For example, García-Moreno and Amat-Guerri et al. reported that novel BODIPY-based polymers were prepared by free-radical copolymerization of methyl methacrylate with BODIPY monomers having the 8-position substituted by long alkyl chains or phenyl groups, tethered with methacryloyloxy groups and exhibited efficient and high photostability toward lasers in liquid solution as well as in solid polymeric matrices.

The first example of BODIPY polymer with a π-conjugated backbone was recently reported by our group.[37] A novel class of rod–coil organoboron polymers with *p*-phenylene–ethynylene as the rod segment and long alkyl chain (decyl group) as the coil segment has been prepared from Sonogashira coupling of BODIPY monomer **10** with bisiodophenyl and decyl groups with various diyne monomers (Figure 5). The characterization by means of scanning electron microscopy (SEM) and transmission electron microscopy (TEM) revealed the strong tendency of the obtained polymers **11**–**13** to self-assemble into particles in solution and cast films on µm–nm scale. Especially, **11** showed the presence of nm-sized particles and µm-sized chain-like structures formed by aggregation of each particle. Further, in CHCl$_3$, the gelation of **11** by three-dimensional aggregation of each fiber was observed at room temperature after 24 h. Their luminescent properties showed high energy-transter efficiency from π-conjugated polymer linkers to BODIPY moieties ($\Phi_F > 71\%$).

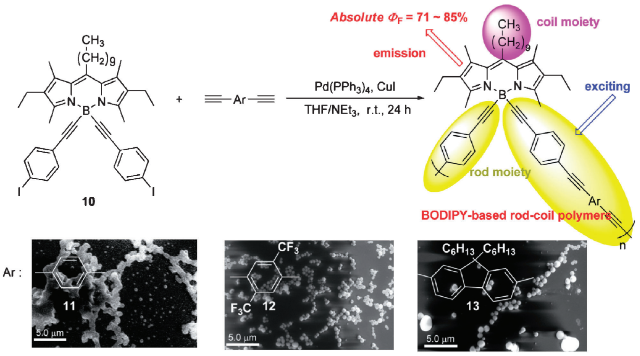
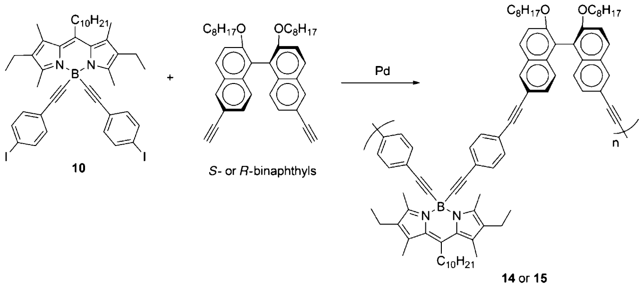


Figure 5. Sonogashira coupling of BODIPY monomer **10** with various diethynyl compounds **11**–**13** and the inset shows SEM images of **11**–**13**.

The intriguing formation of supramolecular self-assemblies leads to a low quantum yield. On the other hand, this aggregation is not suitable for electronic devices. Therefore, we have found quantum yield and morphology controls of BODIPY-conjugated polymers[38] using molecular cognizable inhibitors in a biochemical concept. Islet amyloid fibril formation (IAPP), stabilized by hydrogen bonds, which is involved in devastating diseases such as type-II diabetes mellitus, can be prevented by altering amino acid sequence[39] and using analogs of IAPP methylated at amide bonds[40,41] and small molecules[42,43] as inhibitors, resulting from inhibition by replacement of interaction such as hydrogen bonds and π–π stacking during formation. Inspired by these interesting phenomena, chiral rod–coil organoboron polymers **14** and **15** were prepared from Sonogashira coupling of **10** with *S*- or *R*-6,6′-diethynyl-2,2′-dioctyloxy-1,1′-binaphthyls (Scheme 3). The number-average molecular weights (M_n), measured by size-exclusion chromatography (SEC) in THF, of **14** and **15** were 12100 and 9200, respectively, and the molecular weight distributions (M_w/M_n) of the polymers were very wide ($M_w/M_n > 8.00$), predicting that these wide distributions lead to the formation of supramolecular self-assemble structures, such as particles and fiber, supported by dynamic light scattering (DLS) and SEM measurements. Examining the relationship between the ratio of photoluminescence (PL) intensity ($I/I_0 = \mathbf{15}/\mathbf{14}$) and particle diameter versus **15** content of the mixed polymer of **14** and **15** in THF (Figure 6), which varied from 0 to 100%, the mixed polymer



Scheme 3. Sonogashira coupling of BODIPY monomer **10** with *S*- or *R*-6,6′-diethynyl-2,2′-dioctyloxy-1,1′-binaphthyls.

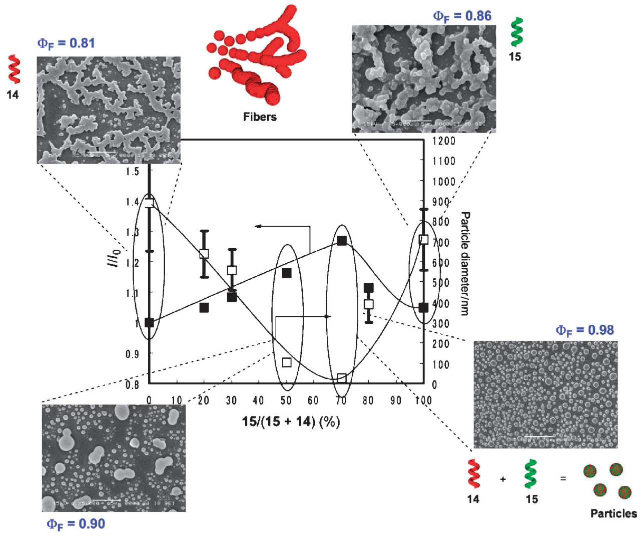
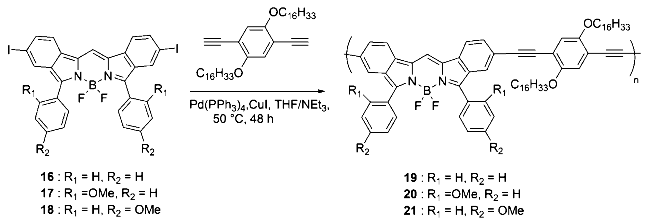


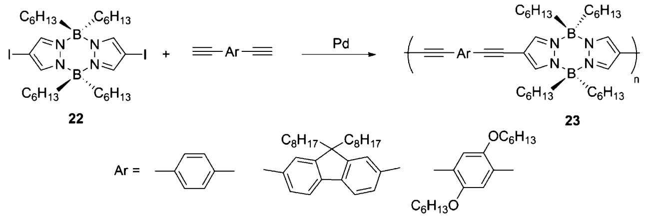
Figure 6. Relationship between **15**/(**14** + **15**) and (emission intensity (I) of **15** at 532 nm)/(emission intensity (I_0) of **14** at 532 nm) in THF (1.0×10^{-5} mol L^{-1}) and particle diameter measured by DLS analysis in THF (8.6×10^{-3} mol L^{-1})] and the inset shows SEM images of the mixed polymers (**14**/**15** = 0/100, 50/50, 30/70, and 100/0).

(**14**/**15** = 30/70) showed complete particle structures from nm to µm sizes, and the quantum yield of the mixed polymer was significantly high (98%). However, such BODIPY-based conjugated polymers **11**–**15** commonly have no red shift of absorption and emission maxima form extended π conjugation, because p-arylene–ethynylene moieties were directly attached to boron atoms. Recently, to improve defective electroproperties, Liu et al. reported synthesis of BODIPY polymeric dyes with emission maxima at 583–683 nm; i.e., the conjugated polymers possessed significant extension of π conjugation by attaching directly to BODIPY cores, with triple bond[44] or fluorene[45] connections between BODIPY cores and aromatic units.

We also succeeded in the synthesis of high near-infrared emissive π-conjugated polymers **19**–**21** with narrow emission bands by incorporation of three monomers based on boron di(iso)indomethene **16**–**18**, which is the introduction of a BODIPY core fused aromatic ring[46] into poly(p-phenylene–ethynylene) backbone.[47] As shown in Scheme 4, three conjugated polymers were synthesized via Sonogashira coupling of 1,4-diethynyl-2,5-dihexadecyloxybenzene and three diiodophenyl-fused BODIPY monomers. The polymers obtained were fusible and soluble in common organic solvents including THF, benzene, toluene, $CHCl_3$, and CH_2Cl_2. The incorporation of the di(iso)indomethene monomers into p-phenylene–ethynylene main chain led to red shifts in UV-absorption and PL spectra by extended π conjugation of the copolymers in comparison with the monomers. Accordingly, the copolymers emit in a range from deep-red to near-infrared with emission spectral maxima at around 691–720 nm and exhibited high quantum yields (Φ_F = 33–49%) in this region.



Scheme 4. Sonogashira coupling reaction of boron di(iso)indomethene-based monomer **16**–**18** with 1,4-diethynyl-2,5-dihexadecyloxybenzene.

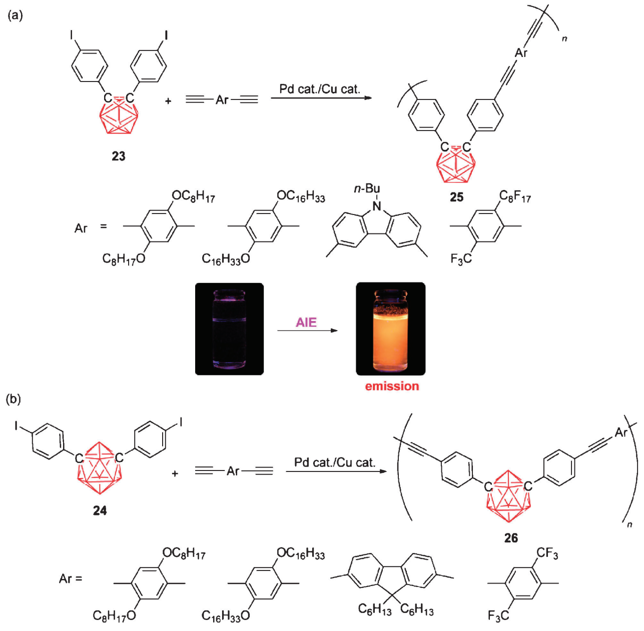


Scheme 5. Sonogashira coupling reaction of 2,6-diisopyrazabole **22** with various dinethynyl compounds.

◆ Pyrazabole

Pyrazabole is a highly stable boron heterocycle in which a variety of functional groups can be readily introduced. Several applications of pyrazaboles have been reported, including their use as possible building blocks for discotic liquid crystals or good bridges for ansa-ferrocenes to form active container molecules for supramolecular applications.[20]

Poly(pyrazabole)s **23** were prepared by organometallic polycondensation of 2,6-diisopyrazabole **22** with aromatic diyne monomers using Sonogashira coupling (Scheme 5).[48] The absorption maxima of the polymers were not particularly red-shifted in comparison with those for aromatic monomers, indicating the π conjugation was poorly expanded via the repeating units. This is due to small electronic interaction between π orbitals of pyrazole. However, optical transparency would be advantageous for various applications as optical materials. The polymers are highly stable against air and moisture, and show purple to green fluorescence emission with good quantum yields when irradiated with UV light. The observed fluorescence emission peaks were composed of multi-emission peaks probably due to various conformations of the pyrazabole units such as flat, boat, and chair. The presence of pyrazabole in the π-conjugated polymer backbone was crucial in the observed emission behavior. Further, incorporation of various electron-withdrawing groups into the main chain leads



Scheme 6. Synthesis of (a) *o*-carborane- and (b) *m*-carborane-based conjugated polymers. The inset shows photographs of **25** in THF and mixed solvent (THF/$H_2O = 1/99$) under UV irradiation (365 nm).

to low electron density on the boron atom, and the fluorescence emission wavelength shifted to shorter wavelength region.[49] Therefore, tuning of emission wavelength was possible by introducing designed aromatic groups having various electron density.

Transition metal-containing poly(pyrazabole)s were also prepared by copper-catalyzed dehydrohalogenation.[50] MLCT absorption was observed only in the case of platinum-containing polymers while such behavior was not for palladium and nickel-containing polymers.

◆ Carborane

Carborane, composed of ten boron atoms and two carbon atoms, is an icosahedral boron cluster potentially useful in the field of medicinal chemistry and material science as a result of rich boron content and high thermal or chemical stability, derived from three-center-two-electron bonds and consequent three-dimensional delocalization of skeleton electrons.[51] The special reactivity and electron-withdrawing nature of carboranes can be regarded as three-dimensional aromaticity.[52] Tour et al. reported *p*-carboranes connected with *p*-phenylene–ethynylene as carborane-wheeled nanocars and showed the occurrence of bathochromic absorption shift, meaning extension of π-conjugation length with incorporation of *p*-carborane.[53]

Recently, a series of *o*-carborane or *m*-carborane π-conjugated polymers **25** and **26** were also prepared through Sonogashira coupling of diiodo-*o*-carborane[54] or diiodo-*m*-carborane[55] monomers **23** and **24** with aromatic diyne monomers (Scheme 6). Bathochromic shifts of absorption maxima of the *o*-carborane or *m*-carborane polymers were observed in dilute solution due to extension of π-conjugation length of the *p*-phenylene–ethynylene segment via *o*-carborane or *m*-carborane moieties in the polymer backbones, respectively. The fluorescence emission of **25** was observed in mixed solvent of tetrahydrofuran/water (1/99 v/v), while the emission of the polymers was not observed in organic solvents, meaning aggregation-induced emission (AIE) in water dispersion. This is the fact that variable C–C bonds in *o*-carborane cluster efficiently quench the fluorescence from *p*-phenylene–ethynylene segments in solution state. In contrast, **26** exhibited intense blue emission in solution state due to no variable C–C bond dissipating the excited states in the solution state. More recently, we reported optically active *o*-carborane-based conjugated polymers sharing both AIE and high order structure such as helical conformation.[56]

◆ Summary

As described above, we have developed various boron π-conjugated polymers by incorporation of stable organoboron complexes into π-conjugated polymer backbones to afford more stable and higher luminescent conjugated polymers than three-coordinated organoboron polymers, which was first reported in 1998. Because it is necessary to enhance their stability and photoproperties for the enormous variety of potential applications. For example, in the field of light-emitting devices, boron π-conjugated polymers are not only intriguing as emitter, but also as electron-transporting materials with high electron affinity. For higher enhancement of their thermal- and photo-stabilites, further studies are under way. In the near future, the industrial applications of organoboron π-conjugated materials will be found via design and unique electronic properties of polymer skeletons.

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