

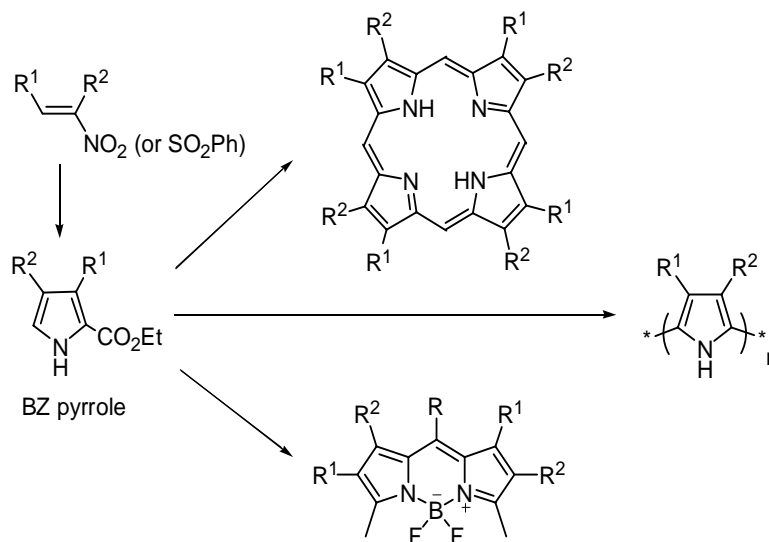
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BARTON-ZARD PYRROLE SYNTHESIS AND ITS APPLICATION TO SYNTHESIS OF PORPHYRINS, POLYPYRROLES, AND DIPYRRROMETHENE DYES

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Abstract – Pyrroles prepared by the reaction of alkyl isocyanoacetates with nitroalkenes or vinylsulfones (Barton-Zard reaction, BZ reaction) are useful for the synthesis of biologically active pyrroles, porphyrins, polypyrroles, and dipyrromethene dyes. This review covers recent development of the BZ reaction and its application to the field of material science.



Pyrroles are important heterocycles, which are found in many natural products and biologically active compounds. The tetrapyrrolic ‘pigments of life’ such as heme, chlorophyll, vitamin B₁₂ and the bile pigments have been active subjects to extensive study in various fields of science.¹ Other many pyrrole-containing natural products are also important as biologically active compounds. For example, over 250 pyrrole-containing compounds are known from marine organisms, lamellarine O, lukianol A,² lamellarin G,³ halitulins⁴ and dictyodendrin⁵. Some of them are molecular targets for selective chemotherapeutic agents for the fight against cancer. Pyrrole alkaloids of the prodigiosin, the deep red

pigment produced by the gram negative bacteria, afford a new series of biologically active compounds.⁶ Thus, pyrroles are key synthetic intermediates for biologically active heterocycles.⁷ Furthermore, pyrroles are important as key components in material science, namely, pyrroles are contained in conductive polymers,⁸ semiconductors for application to organic electronics,⁹ and synthetic dyes for application to opt electronics and photodynamic therapy.¹⁰

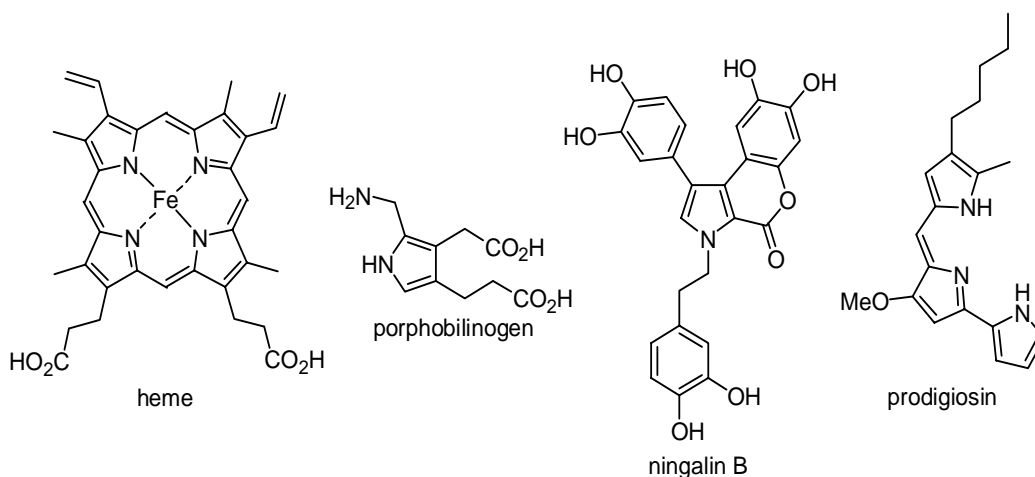
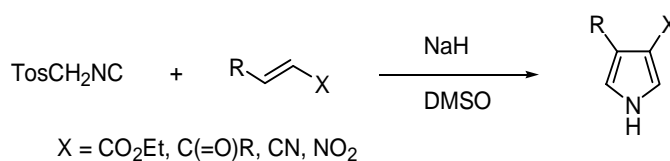


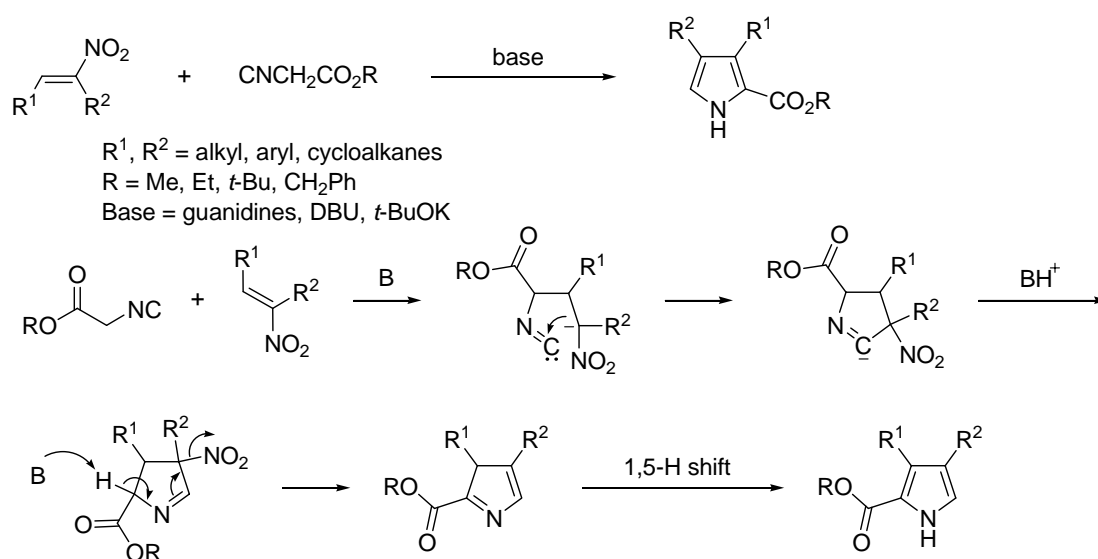
Figure 1 Biologically Active Pyrroles



Scheme 1 Van Leusen Reaction

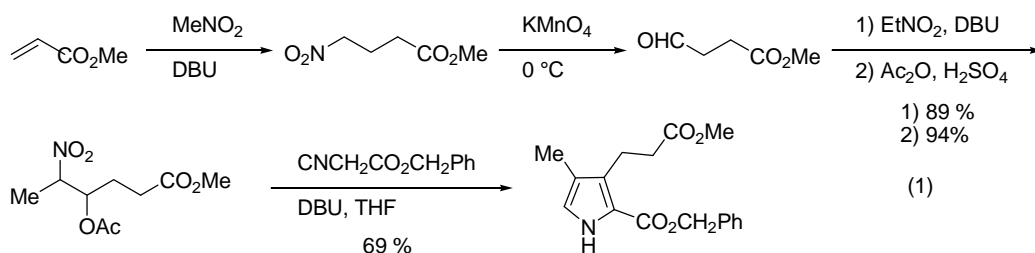
There are many methods to construct pyrrole rings from open-chain precursors. Cyclization and cycloaddition are two main routes to get them.¹¹ The Knorr, Hantzsch, Paal-Knorr, and Piloty-Robinson reactions are very famous for pyrrole synthesis via cyclization.¹² These reactions have been used for long time, but still subjected to many investigations and modifications. Recently Buchwald reported a highly efficient synthesis of pyrrole with a wide variety of functional groups utilizing a Cu-catalyzed tandem C-N bond-forming reaction of 1,4-dihalo-1,3-dienes.¹³ Compared to such traditional reactions, the isonitrile cyclization reactions have been developed in recent years. The isonitrile cyclization reactions provide heterocycles with substitution patterns which are not easily available by other methods. For example, *p*-tolylsulfonylethylisocyanide (TosMIC) reacts with aldehydes or electron deficient alkenes in the presence of a base to give oxazoles or pyrroles, respectively. TosMIC is now well known as van Leusen reagent and has been widely used in organic synthesis.^{14a} Pyrrole synthesis using TosMIC is shown in Scheme 1. This method is very attractive, for α -free pyrroles are obtained in one step, for example, the reaction of nitroalkenes with TosMIC gives 3-nitropyrroles in 55-85% yields.^{14b,14c}

In 1985, Barton and Zard reported that the base-catalyzed reaction of nitroalkenes or β -nitro acetates with alkyl isocyanoacetates gave pyrrole-2-carboxylates (Scheme 2).¹⁵ The nitro group acts as an activating group for the C-C bond formation process and a leaving group in a pyrrole forming step. This type of pyrrole synthesis is now widely called as the Barton-Zard reaction (BZ reaction), and it has become an important method for the pyrrole synthesis.



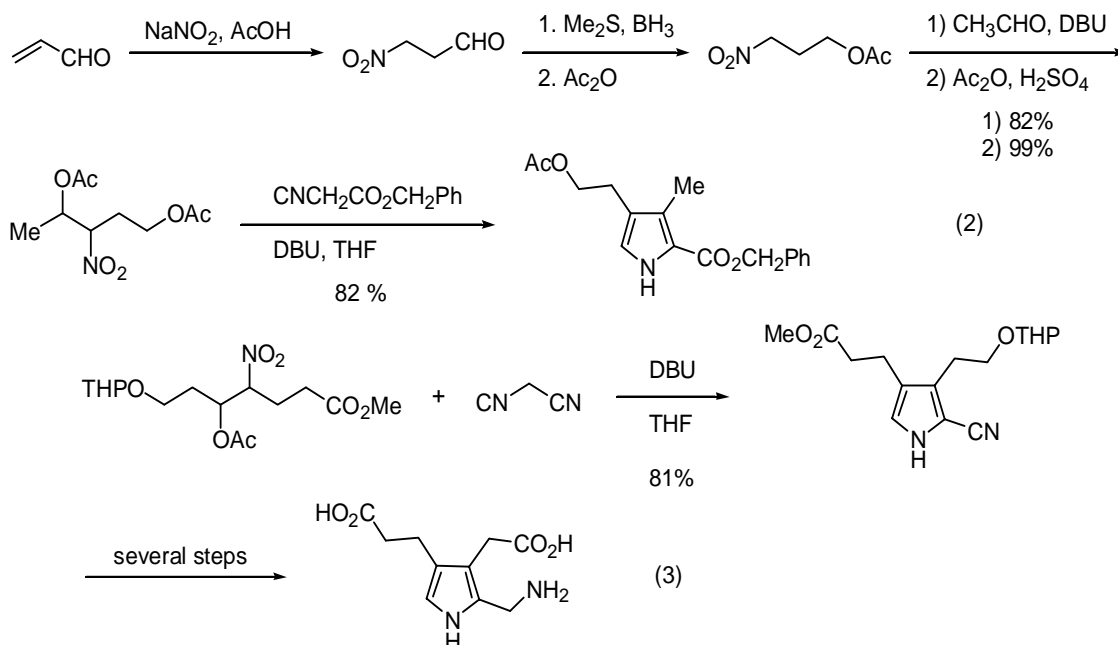
Scheme 2 Barton Zard Reaction

CHAPTER 1 BARTON-ZARD REACTION (BZ REACTION)

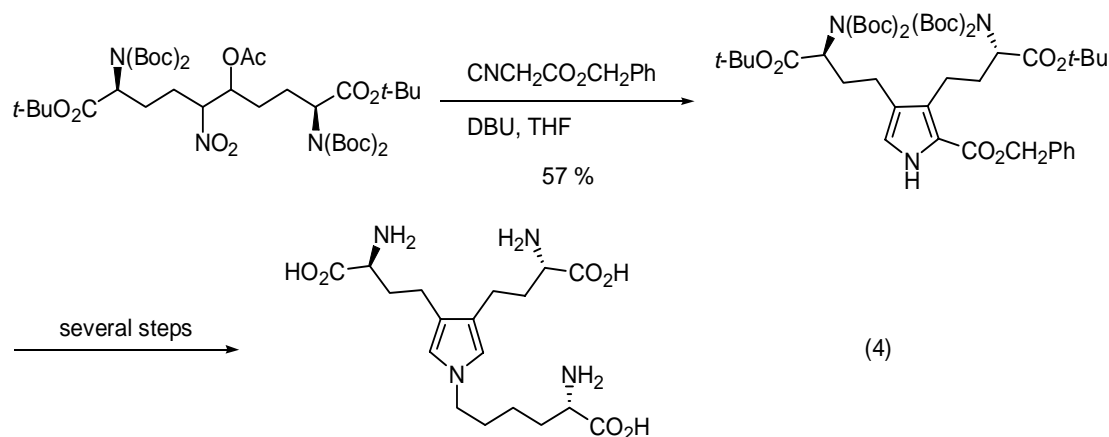


The advantage of the BZ reaction over other methods is that various groups are readily introduced into 3 and 4-positions of pyrrole-2-carboxylates by a simple procedure. As nitroalkenes are prepared by the various methods such as nitroaldol reaction or nitration of alkenes,^{16, 17} pyrroles with various groups at the 3- and 4-positions are available. Furthermore, the reaction proceeds very cleanly, so that polymer-supported reagents can be used to generate array of 1,2,3,4-tetrasubstituted pyrroles derivatives without any chromatographic purification step.¹⁸ Convenience of the BZ reaction is well demonstrated in eq 1 and 2.¹⁹ The Michael addition of nitro compounds, Nef reaction, and nitro-aldol reaction are sequentially used to get the requisite β -nitro acetates for the BZ reaction.

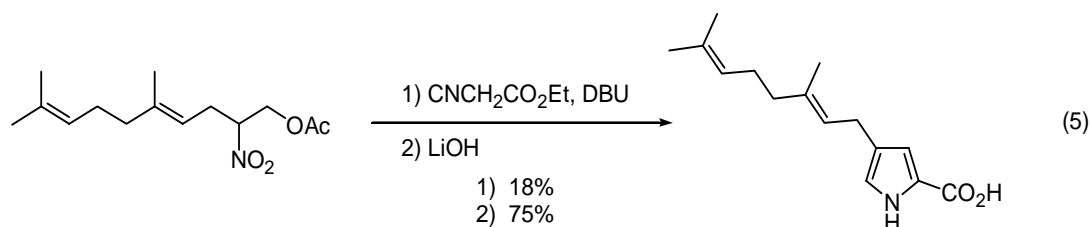
The BZ reaction has now been extensively applied to synthesis of biologically active pyrroles. For example, porphobilinogen, which is the key building block in the pigments of life such as heme and vitamin B₁₂, is prepared via the BZ reaction as shown in eq 3.²⁰



Another application of the BZ reaction to biologically active compounds is demonstrated in eq 4, where (+)-deoxypyrrolorine, a potential biochemical marker for diagnosis of osteoporosis is prepared by using the BZ reaction.²¹ Osteoporosis is a crippling degenerative bone disease that affects the aged population, particularly postmenopausal women.



Pyrrostatin is a novel lipid per oxidation inhibitor, which consists of a pyrrole-2-carboxylic acid with geranyl group at the 4 position. It is readily prepared by applying the BZ reaction as shown in eq 5.²²



Phytochrome is a chromoproteins concerned in a variety of higher plants such as growth, development, and morphogenesis.^{1b} Total synthesis of phytochromobilin and related compounds has been achieved by Inomata and his coworkers to understand their biological activity, where the BZ reaction has been used for the preparation of the requisite pyrrole rings.²³ Side chains such as methyl, vinyl, ethyl, and propionic acid are readily introduced by the application of nitro-aldol reaction and the subsequent BZ reaction as shown in eq 1 and 2.

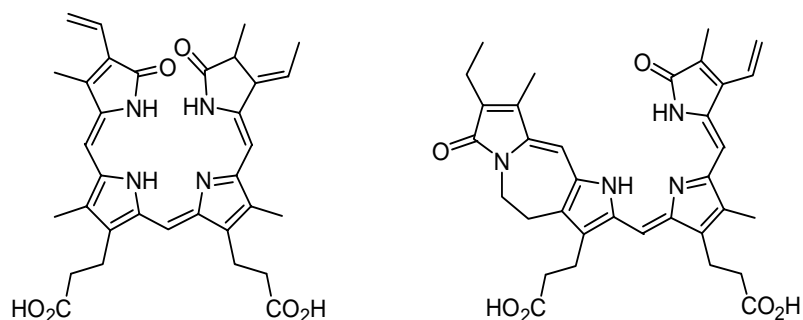
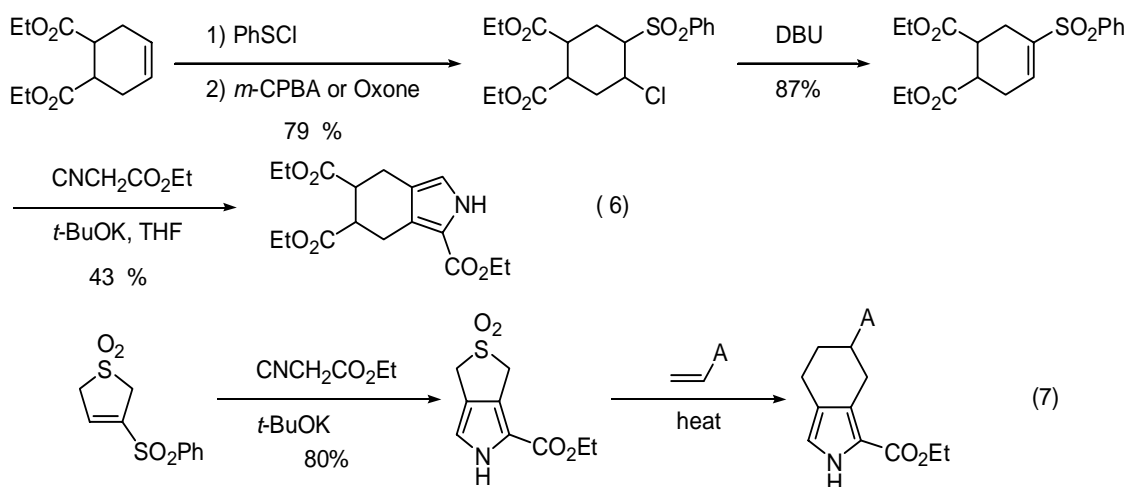


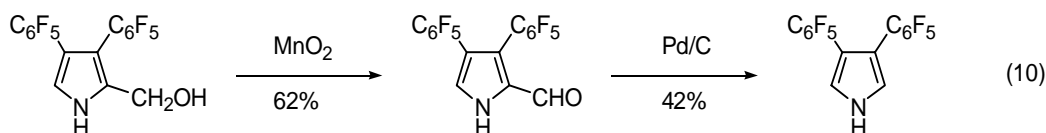
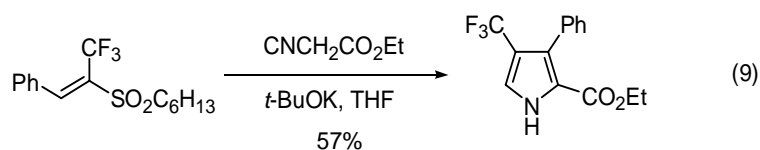
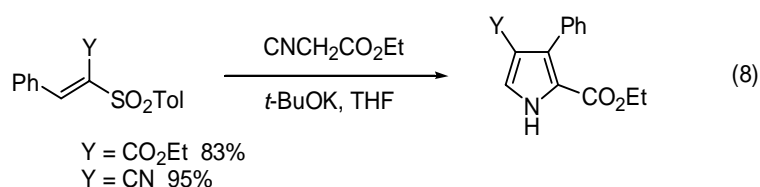
Figure 2 Phytochromobilin and Related Compounds

α,β -Unsaturated sulfones can be used instead of nitroalkenes for the BZ reaction. Montforts and his coworkers have developed the preparation of pyrroles by this route. As alkenes are readily converted into α,β -unsaturated sulfones via the addition of phenylsulfenyl chloride followed by oxidation of the sulfides to the sulfones and elimination of HCl, the BZ reaction using α,β -unsaturated sulfones are useful for the preparation of pyrroles from alkenes. The BZ reaction using α,β -unsaturated sulfones is carried out in the presence of *t*-BuOK in THF to give pyrroles in reasonable yields (eq 6).²⁴ The BZ reaction of 1-phenylsulfonyl-3-sulfolene affords 3,4-fused pyrrolo-3-sulfolenes,²⁵ which undergo the Diels-Alder reaction with various dienophiles such as electron deficient alkenes involving C₆₀.²⁶

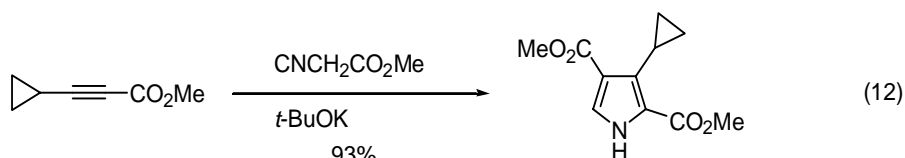
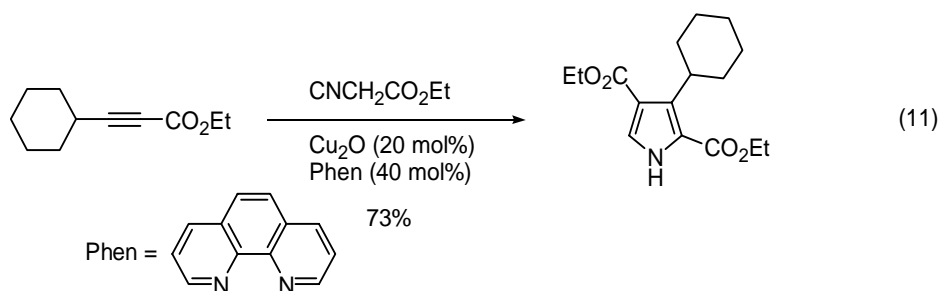


The BZ reaction using α,β -unsaturated sulfones is especially useful for the preparation of pyrrole-2-carboxylates with electron-withdrawing groups at the 4-position. For example, CF₃, CN, and CO₂R are readily introduced into the β -position of pyrroles in good yields by this process as shown in eq 8 and 9.²⁷

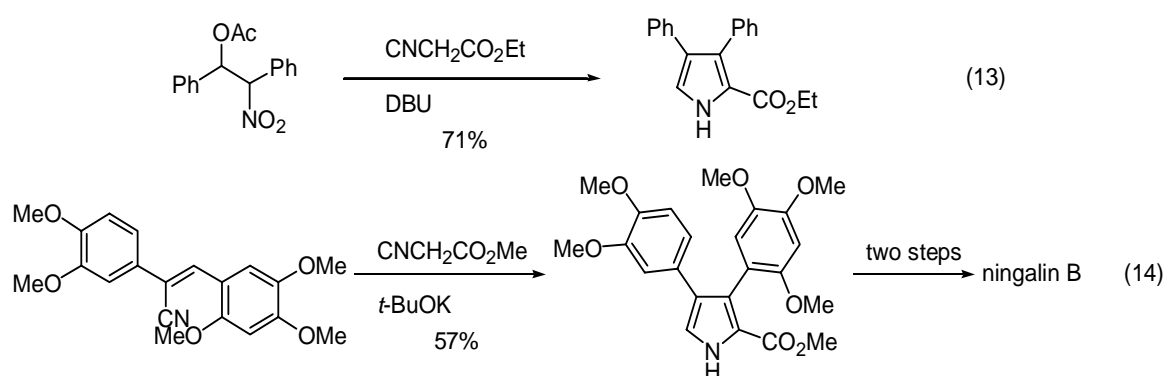
The choice of base for the BZ reaction depends on the reactivity of electron deficient alkenes. DBU is reactive enough in the reaction with nitroalkenes, but a stronger base such as *t*-BuOK is required in the reaction of α,β -unsaturated sulfones in eq 6 and 7. As two electron withdrawing groups are presented in eq 8, DBU gives pyrroles in good yields. When nonionic strong base, *t*-butyliminotris(pyrrolidino)phosphorane (BTPP), is employed in the reaction of eq 9, the yield is increased to 79 %. When Y is F in eq 8, the yield of 4-fluoropyrrole-2-carboxylate is poor due to the formation of by-products.²⁸ Pyrroles with C₆F₅ at β -positions are prepared by the BZ reaction of α,β -unsaturated sulfones with C₆F₅ groups followed by reduction with LiAlH₄, oxidation with MnO₂ and decarbonylation with Pd/C (eq 10).²⁹



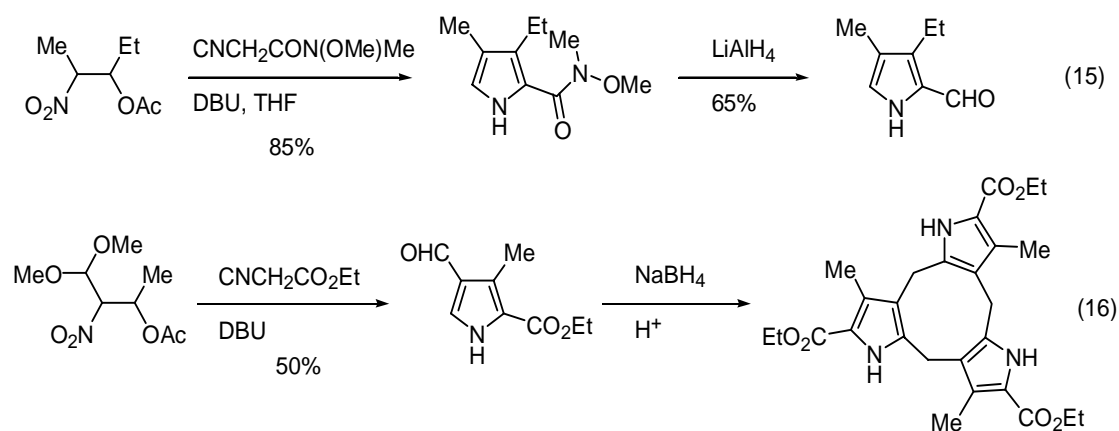
Recently, Yamamoto³⁰ and de Meijere,³¹ independently, reported that pyrrole-2-carboxylate with electron withdrawing groups can be directly prepared by the reaction of alkyl isocyanoacetates with electron-deficient alkynes as shown in eq 11 and eq 12. They belong to the BZ reaction, where the leaving group (sulfonyl group) is not required. Although the sulfonyl groups are required in the reaction of eq 8, it proceeds more rapidly than those in eq 11 and 12. As the requisite α,β -unsaturated sulfones are readily prepared by the Knoevenagel or related reactions from aldehydes, the choice of these reactions depends on the availability of alkynes or aldehydes.



3,4-Diarylpyrroles are important in the synthesis of pyrrole alkaloids or porphyrins with altered electronic properties. They are readily prepared by the BZ reaction using nitroalkenes (eq 13).³² However, the requisite α -nitrostilbenes or their equivalents are not easy to prepare in some cases. Interestingly, α,β -unsaturated nitriles can be used instead of nitroalkenes in the preparation of 3,4-diarylpyrroles (eq 14).³³ The marine natural products such as Ningalin B (see Figure 1) are readily prepared by this methodology. Recently, Anderson used this reaction for the preparation of 3,4-diarylpyrrole-2-carboxylate as a starting material of dodecaarylporphyrin, where aryl is 4-iodo-3-alkoxyphenyl group.³⁴



Pyrrole-2-carbaldehydes are important building blocks in the synthesis of oligopyrrolic macro cycles such as porphyrins and linear oligopyrroles. Such formyl pyrroles are generally prepared by the Vilsmeier-Haak reaction of α -free pyrroles. As an alternative method, the ester group of the BZ reaction product is converted into a formyl group via reduction and oxidation as shown in eq 10. The BZ reaction of isocyanide substituted with Weinreb amide with nitroalkenes followed by reduction with LiAlH_4 gives an excellent method for the preparation of pyrrole-2-carbaldehyde (eq 15).³⁵



4-Formyl pyrrole-2-carboxylates can be prepared by the BZ reaction using nitroacetaldehyde dimethylacetal as shown in eq 16.³⁶ Thus, formyl group can be introduced at the 2- or 4-position regioselectively by the BZ reaction. The 4-formyl group is reduced to 4-hydroxymethyl group with NaBH_4 , which is replaced by various nucleophiles such as RSH or ROH . Internal cyclization of

4-hydroxymethylpyrrole gives bowl-shaped cyclononatripyrroles, which adopt crown conformation in solution.³⁶ 3-Alkanoyl pyrroles are also prepared by the similar procedures.³⁷

Ketene *S,S*- and *N,S*-acetals with electron withdrawing group are also employed in the BZ reaction, where methylthio group is eliminated to form pyrroles with electron withdrawing groups (NO₂, CN, CO₂R) at the 4 position shown in eq 17.³⁸

Other examples of the pyrroles prepared by the BZ reaction are summarized in Figure 3, where the pyrrole has long alkyl groups, CF₃ group, sugar molecules, and naphthyl groups. The last pyrrole has chirality, it is separated to an axially dissymmetric pyrrole.³⁹⁻⁴²

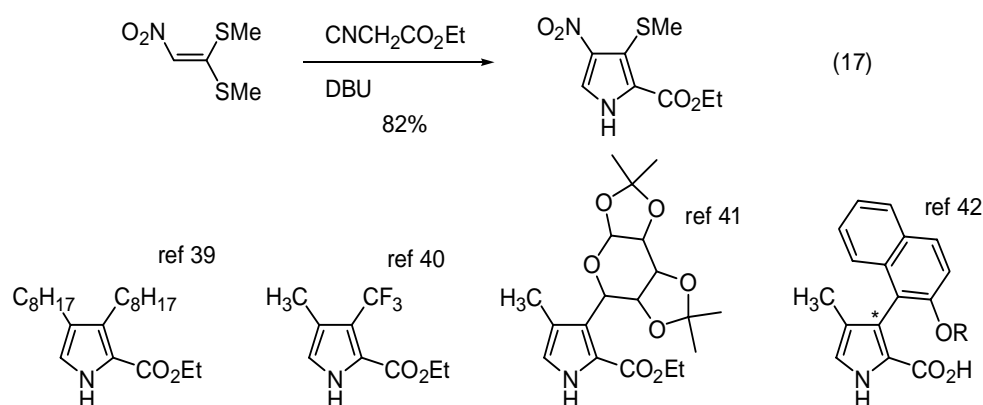
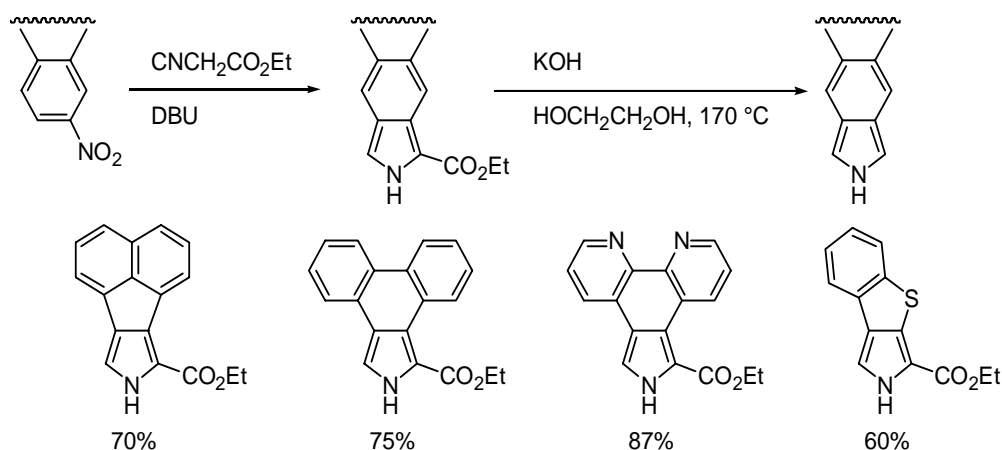


Figure 3 Some Examples Prepared by the BZ reaction

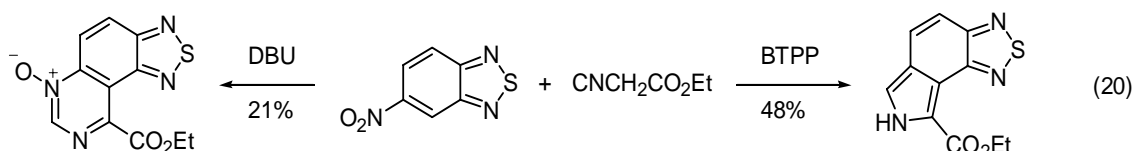
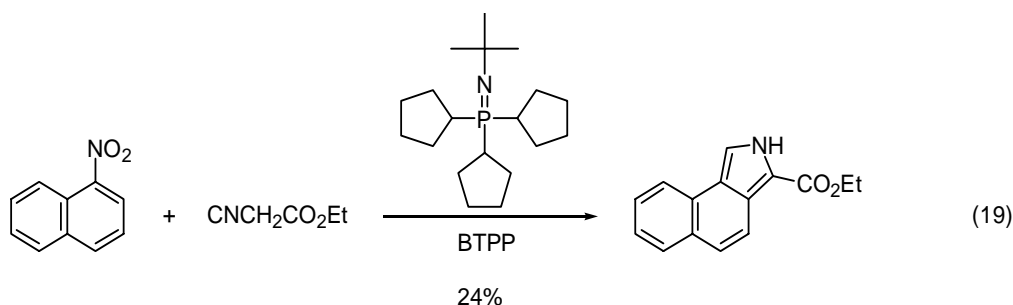
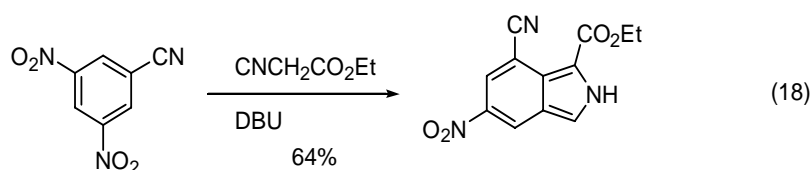
In 1994, we found that certain aromatic nitro compounds are reactive enough to undergo the BZ reaction. For instance, polycyclic aromatic nitro compounds are generally reactive toward the anion of ethyl isocyanoacetate to give pyrroles fused with polycyclic aromatic rings.⁴³ Ethoxycarbonyl group is readily removed by heating with KOH in ethylene glycol to give α -free pyrroles. Independently, Lash and his coworkers have developed the same strategy to prepare the pyrroles fused with exocyclic rings such as phenanthropyrroles and phenanthrolinopyrroles by the same procedure.⁴⁴



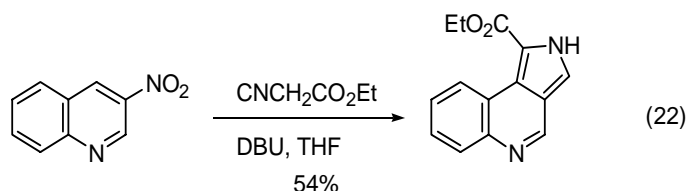
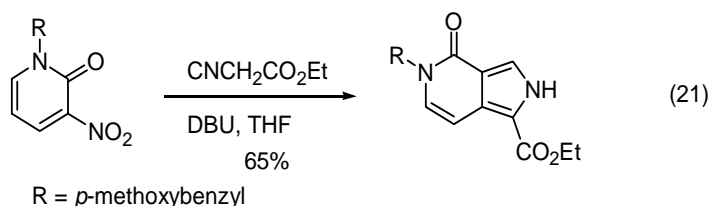
Scheme 3 Pyrroles Fused with Aromatic Rings

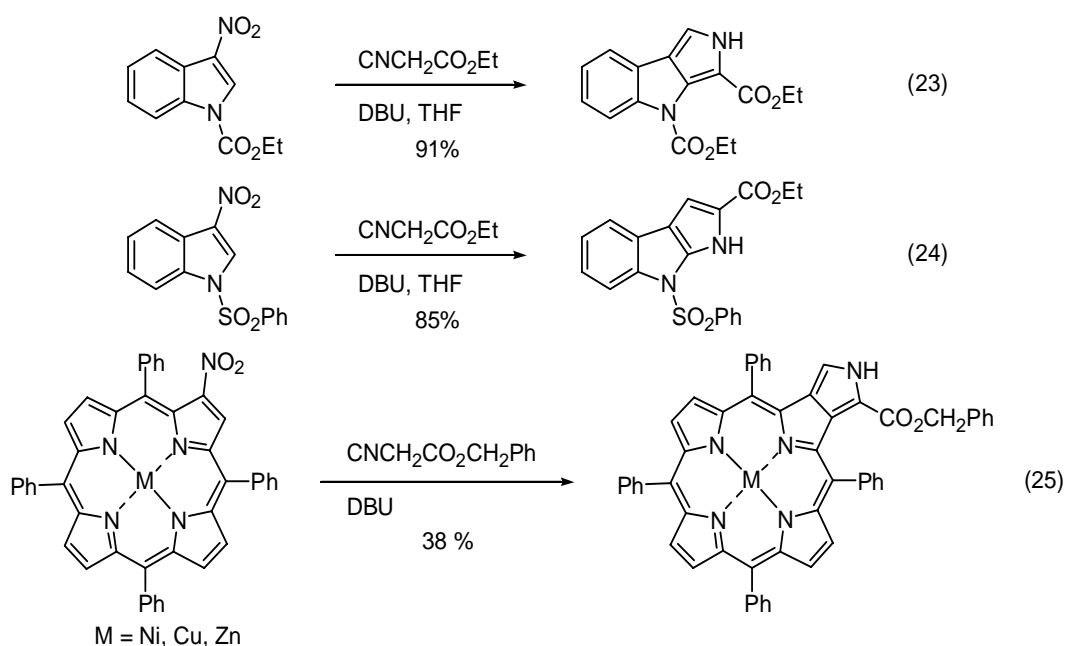
The method using aromatic nitro compounds in the BZ reaction is very attractive, for aromatic nitro compounds are readily prepared by the nitration of aromatic compounds. However, nitrobenzene itself is

not reactive enough to give isoindole by BZ reaction. Monocyclic nitro compounds such as *m*-dinitrobenzene and its derivatives give isoindole derivatives directly by the BZ reaction. (eq 18)⁴⁵ We found that super strong nonionic base such as BTTP are effective to induce the BZ reaction of 1-nitronaphthalene to give isoindole in 24 % yield, while the DBU catalyzed reaction gives the same product in 2 % yield. (eq 19)⁴⁶ In some cases where DBU fails or gives non-pyrrolic products, BTTP gives pyrroles as shown in eq 20.⁴⁶ The use of BTTP as a base expands scope and limitation of the BZ reaction of aromatic nitro compounds.^{46,47}

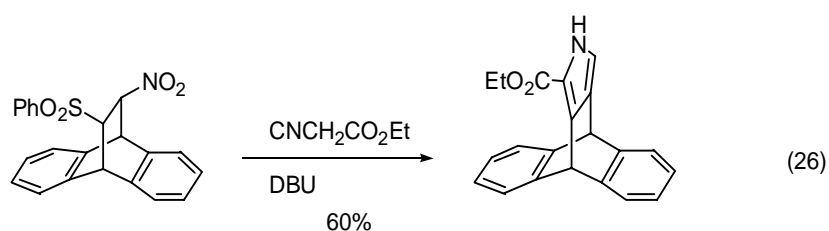


The BZ reaction can be applied to various heterocyclic nitro compounds to give isoindole derivatives, which are difficult to prepare by other methods. Some examples are presented in eq 21,⁴⁸ 22,⁴⁸ 23,⁴⁹ and 24.⁴⁹ The 3-nitroindoles show interesting reactivity toward the anion of ethyl isocynoacetate; *N*-alkoxycarbonyl derivatives give the normal product, the pyrrolo[3,4-*b*]indole ring system (eq 23). On the other hand, *N*-sulfonyl derivatives give the pyrrolo[2,3-*b*]indole ring system (eq 24). β -Nitroporphyrins also undergo the BZ reaction to afford fused pyrroloporphyrins as shown in eq 25, which are useful precursors for highly conjugated porphyrin oligomers.⁵⁰





The combination of the Diels-Alder reaction of β -sulfonylnitroethylene and the BZ reaction provides a new synthesis of pyrroles fused with polycyclic skeleton (eq 26).⁵¹ β -Sulfonylnitroethylene can be replaced by bis-1,2-sulfonylethylene or sulfonylacetylene as discussed later.



The base catalyzed reaction of nitroalkenes or nitro aromatic compounds with ethyl isocyanoacetate does not afford always pyrroles but affords pyrimidine or pyrazoles in some cases as listed in Figure 4.

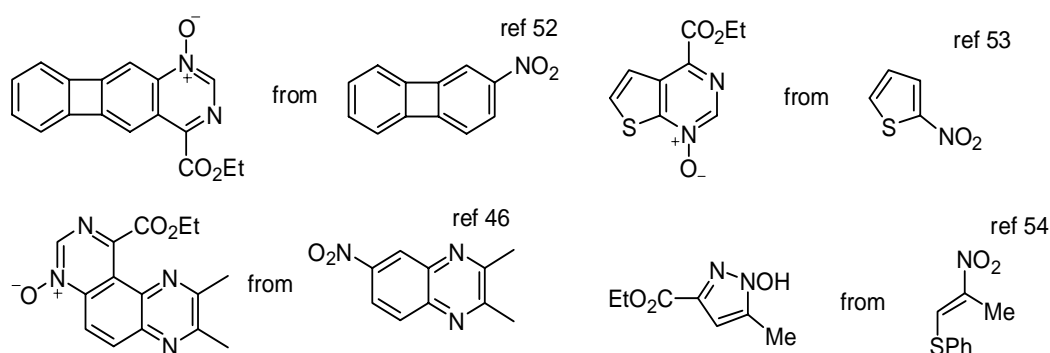
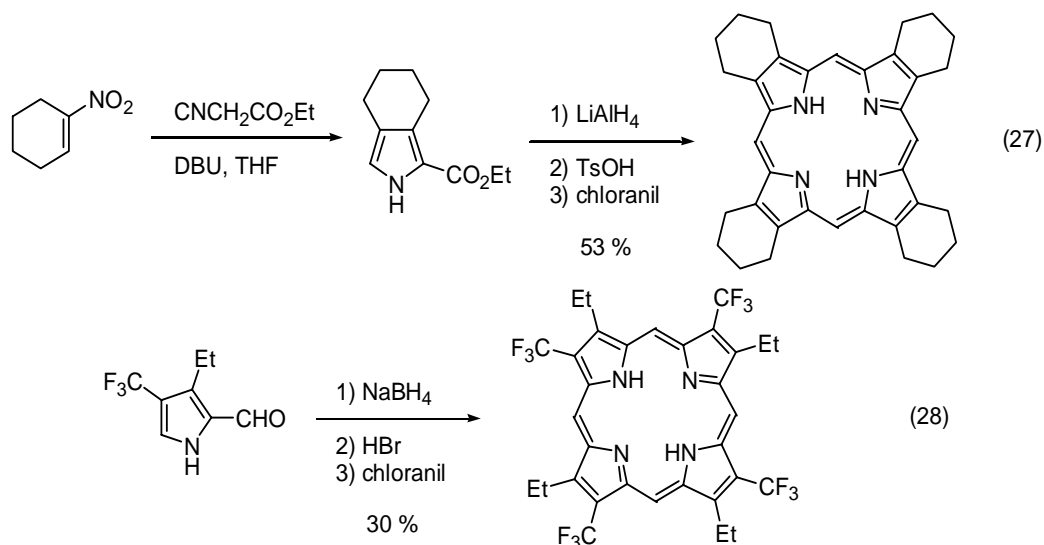


Figure 4 Unusual Products via the BZ reaction

CHAPTER 2 SYNTHESIS OF PORPHYRINS

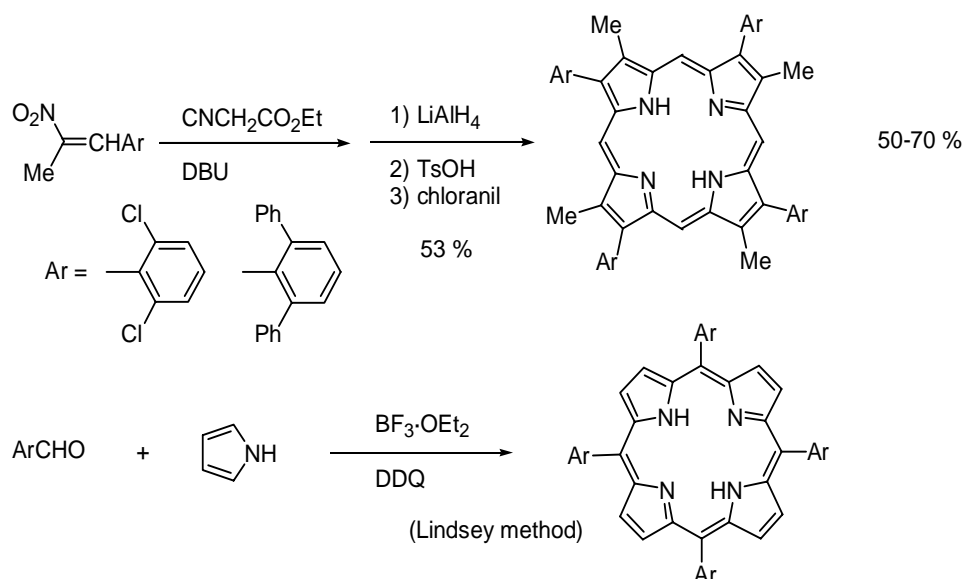
In 1985 we reported a new method for conversion of pyrrole-2-carboxylates into porphyrins as shown in eq 27.⁵⁵ The procedure is very simple, 1) LiAlH₄, 2) H⁺, 3) oxidation, which is now a standard protocol in porphyrin synthesis. Another example is synthesis of 2,3,7,8,12,13,17,18-octaethylporphyrin (OEP) that

is important as a standard porphyrin in porphyrin chemistry. Although OEP is commercially available, it is very expensive due to difficulty of the synthesis of it. Now it is readily prepared in 50-70 % yield by the similar procedure of eq 27, where the requisite nitroalkene are prepared from 1-nitropropane and propanal.⁵⁶ OEP is also prepared in 66% yield by the reaction of 3,4-diethylpyrrole with formaldehyde. Experimental details of synthesis of 3,4-diethylpyrrole-2-carboxylate and conversion into porphyrin via 3,4-diethylpyrrole are described in organic synthesis.⁵⁷ As discussed in the chapter 1, the BZ reaction affords various pyrrole-2-carboxylates, the procedure of the eq 27 is very effective for porphyrin synthesis. When substituents at the 3- and 4-positions are not identical, four possible isomers, Type I, Type II, Type III, and Type IV are formed. However, when one of substituents is strong electron withdrawing groups such as CF₃ or NO₂, Type I is formed selectively as shown in eq 28.^{40,58,59} 2,3,7,8,12,13,17,18-Octamethylthioporphyrin^{60,61} is also prepared by the tetramerization of 2-hydroxymethylpyrrole. As such electron deficient pyrroles are not reactive enough to give the corresponding porphyrins by the acid catalyzed reaction with HCHO, the route via 2-hydroxymethylpyrrole is useful for the preparation of such electron deficient porphyrins.

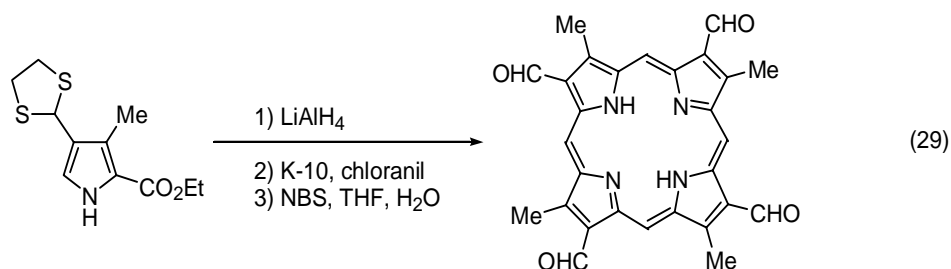


Metalloporphyrins are important as model systems in biologically important co-enzymes such as p-450.⁶² *meso*-Tetraarylporphyrins are widely used for this purpose due to the simplicity of synthesis. They are easily prepared by the reaction of pyrroles with substituted benzaldehydes (Lindsey method).⁶³ However, β -substituted porphyrins are more appropriate model compounds due to their substitution patterns and homology to the heme cofactor. The porphyrin synthesis based on the BZ reaction provides an excellent method for the preparation of β -substituted and *meso*-free porphyrins. For example, 2,7,12,17-tetraarylporphyrins are readily prepared from the pyrrole prepared by the BZ reaction of nitroalkenes derived from ArCHO and nitroethane as shown in Scheme 4.^{56,64} When aryl is a bulky group, type 1 is formed selectively by this method. When ArCHO is 2,6-diphenylbenzaldehyde, the BZ reaction using DBU as a base does not to give the pyrrole in reasonable yield, and BTTPP is required as a base to

get it.⁶⁴ Oxoiron(IV) porphyrin π -cation radicals are believed to participate in the biochemical oxidation such as horseradish peroxidase and catalase. Iron complexes of porphyrins substituted with a bulky group at β - or *meso*-positions and their oxidized species provide a good model of such systems.^{65,66,67} EPR and UV-Vis spectrum of these model compounds derived from β -substituted porphyrins are strikingly similar to those of compound I of natural catalase and peroxidase. Some natural porphyrins contain a β -formyl group, which needs to control the oxidation potential of metalloporphyrins. β -Formyl pyrrole prepared by eq 16 is converted into the corresponding tetraformyl porphyrin via ethyl 4-(dithiolan-2-yl)-3-methylpyrrole-2-carboxylate as shown in eq 29.⁶⁸ β -Monoformyl porphyrin is also prepared by a stepwise process, which may be important as a model of cytochrome C oxidase.

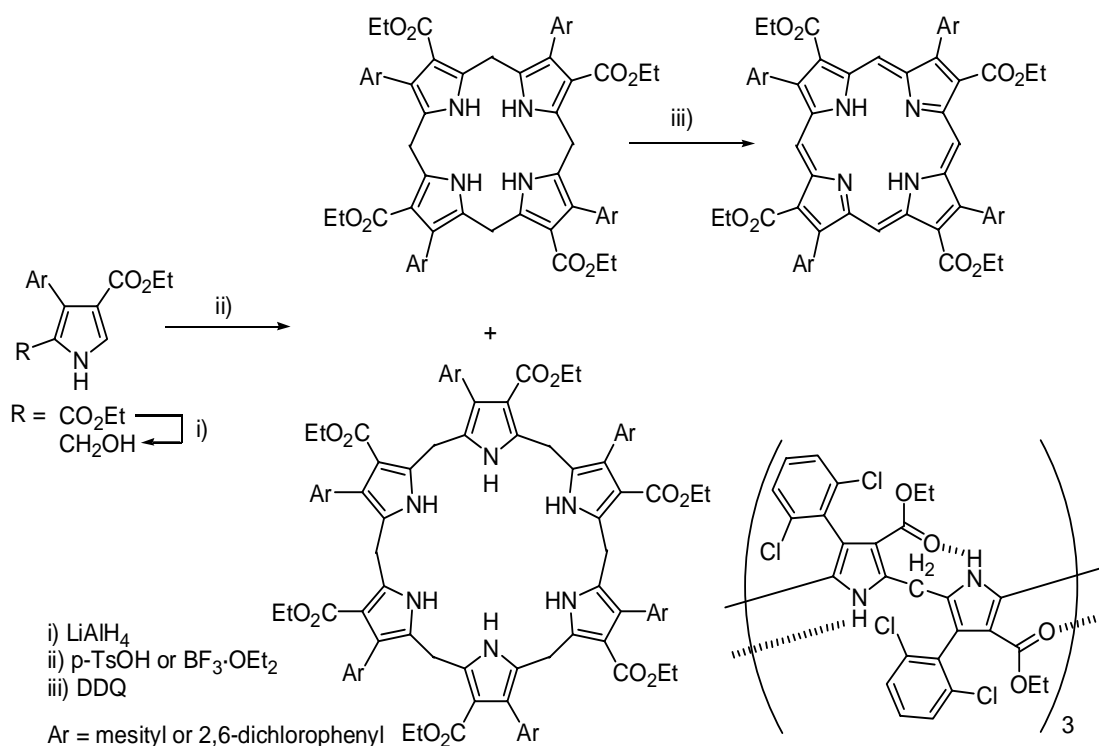


Scheme 4 Synthesis of β -Aryl and *meso*-Arylporphyrins



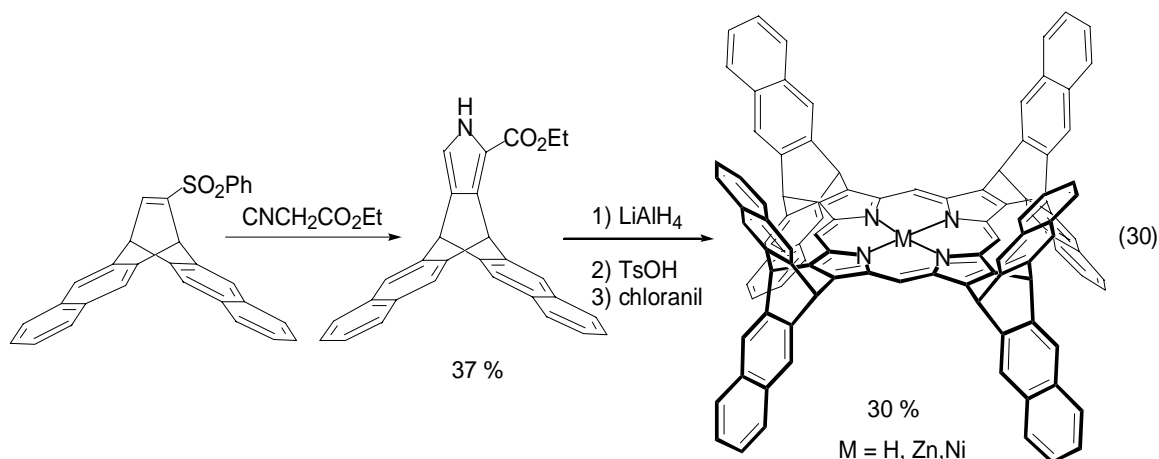
Pyrroles with electron withdrawing groups are readily prepared by the BZ reaction of eq 8, which are all converted into the corresponding porphyrins by a standard procedure (LiAlH_4 , H^+ , and oxidation). For example, reduction of 3-aryl-2,4-diethoxycarbonylpyrroles with LiAlH_4 gives 3-aryl-2-hydroxymethyl-4-ethoxycarbonylpyrroles selectively, which affords porphyrinogenes on treatment with acids. In some cases, hexaphyrinogenes are also isolated. They are intermediates to porphyrins or hexaphyrins, but they are not generally isolated under aerobic conditions. However, porphyrinogenes and hexaphyrinogenes are isolated in the presence of β -ethoxycarbonyl groups. Porphyrinogenes are oxidized to the corresponding porphyrins on treatment with DDQ, but

hexaphyrinogenes are very stable under the conditions using DDQ as shown in Scheme 5.⁶⁹ The strong intramolecular hydrogen bonding between C=O and NH keeps a rigid framework of hexaphyrinogenes, which are confirmed by the X-ray analysis, this is the first case of the isolation of stable hexaphyrinogenes. As hexaphyrinogenes are stabilized by hydrogen bond with β -ethoxycarbonyl groups, pyrroles with other electron withdrawing groups (such as C_6F_5 , CF_3) do not give hexaphyrinogenes but give porphyrinogenes selectively, which are all oxidized to the corresponding electron deficient porphyrins.⁷⁰ This method is useful for the preparation of electron deficient porphyrins.



Scheme 5 Synthesis of Porphyrinogen and Hexaphyrinogen

The Diels-Alder reaction of acenes such as anthracene or pentacene with appropriate dienophiles, followed by the BZ reaction and the conversion into porphyrins provides a unique porphyrin framework, which has a deep cavity.⁷¹ Such porphyrins with well-defined cavities may find their utility as enzyme models and size selective molecular recognition.



Extension of the porphyrin conjugation induces strong absorption in the far-red region of the visible spectrum. Such highly conjugated porphyrins have been pursued by many research groups, for they are important as materials for non-linear optical materials, sensors, and sensitizers of photodynamic therapy.^{10b,72} This has been accomplished by a variety of methods including expansion of conjugated core such as sapphyrins,⁷³ hexaphyrins, heptaphyrins or other higher homologues.^{1c,74} Other approaches are porphyrin oligomers connected with conjugated systems such as triple bonds⁷⁵ or directly fused porphyrin oligomers.⁷⁶ The use of pyrroles fused with aromatic rings is also useful approach for extension of porphyrin conjugation. Such pyrroles are prepared by the BZ reaction using aromatic nitro compounds (except for nitrobenzene) as shown in Scheme 3. A new series of conjugated porphyrins has been prepared by this strategy using polycyclic aromatic nitro compounds in Ono⁵³ and Lash⁷⁷ groups, independently. As good review of this subject is available,⁷⁸ duplication is minimized in this review. Effectiveness of this approach to induce the red-shift of absorption as shown in Figure 5, the Soret band of OEP appears about 400 nm, but the Soret band is shifted to about 500 nm in the tetraacenaphthoporphyrin.^{53,77} As the latter porphyrin is insoluble, the cationic species are measured in TFA-CHCl₃. Protonation is induced the red shift of the absorption by less than 10 nm, so this large red-shift of absorption is mainly due to the fused aromatic rings. Introduction of aryl groups at the *meso*-positions of this porphyrin induces the deformation of the porphyrin ring to increase the solubility.⁷⁷ Lash and his coworkers have prepared a series of tetraacenaphthoporphyrins with *meso*-aryl groups, which exhibit highly red-shifted absorption spectra.⁷⁹ The Soret band appears at 556 nm, and they claim that the unusual red-shift is due to a special effect of an acenaphthylene group. Shen and her coworkers have reported that the absorption of series of *meso*-tetraaryltetraphenathroporphyrin is more red-shifted than those of acenaphthoporphyrins.⁸⁰ Thus, there are no special meanings of acenaphthylene rings in their red-shifted absorption of porphyrins. Recently, this unusual red-shift of these non-planar porphyrins is subjected to theoretical calculations, and it becomes clear that the red shifted absorption of porphyrins in Figure 5 is due to the non-planarity of porphyrins to raise the HOMO energy and conjugation between phenyl and expanded porphyrin rings.⁸¹ Lash and his coworkers have prepared porphyrins with various kinds of exocyclic rings, which are derived from the BZ reaction. As numbers, positions and kinds of exocyclic rings affect the electronic properties of porphyrins, this strategy affords a very effective method to control the HOMO and LUMO energy levels of porphyrins. Porphyrins prepared by this strategy are listed in Figure 6. They use the McDonald [2 + 2] or [3 + 1] condensation of pyrrole units to get the porphyrins.

Limitation of the BZ reaction is that nitrobenzene or 2-nitronaphthalene does not give the isoindole or naphtho[2,3-*c*]pyrrole, respectively. In general, such isoindole derivatives are difficult to prepare owing to their instability. We have found a simple solution of this problem.^{87,88} The pyrrole fused with

bicyclo[2.2.2]octadiene (BCOD) prepared by the BZ reaction can be used as a masked isoindole, for it gives isoindole by heating via the retro Diels-Alder reaction. For example, tetrabenzoporphyrin (TBP) and its metal complexes are prepared by this method (eq 31). Pyrrole fused with BCOD is converted into bicyclo-fused porphyrin (BCODP) in 50-80 % yield by a standard method (LiAlH_4 , H^+ , oxidation). As BCODP is soluble in organic solvents, it can be purified by column chromatography to give a pure sample (purity is 99.9% estimated by HPLC), which is converted into pure TBP in quantitative yield by heating at 180-200 °C. Thus, insoluble TBP is prepared in a highly pure form by this thermal process.

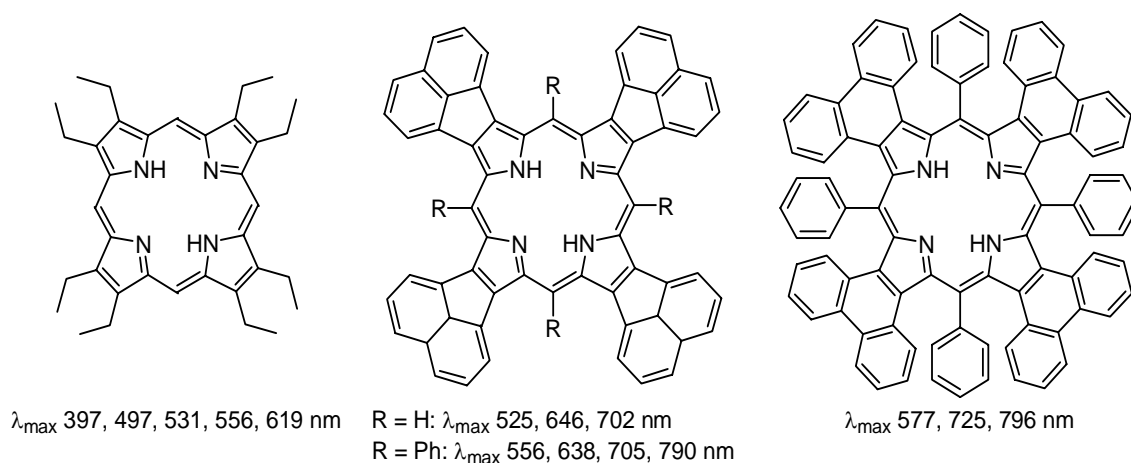


Figure 5 Absorption Spectra of OEP and Expanded Porphyrins

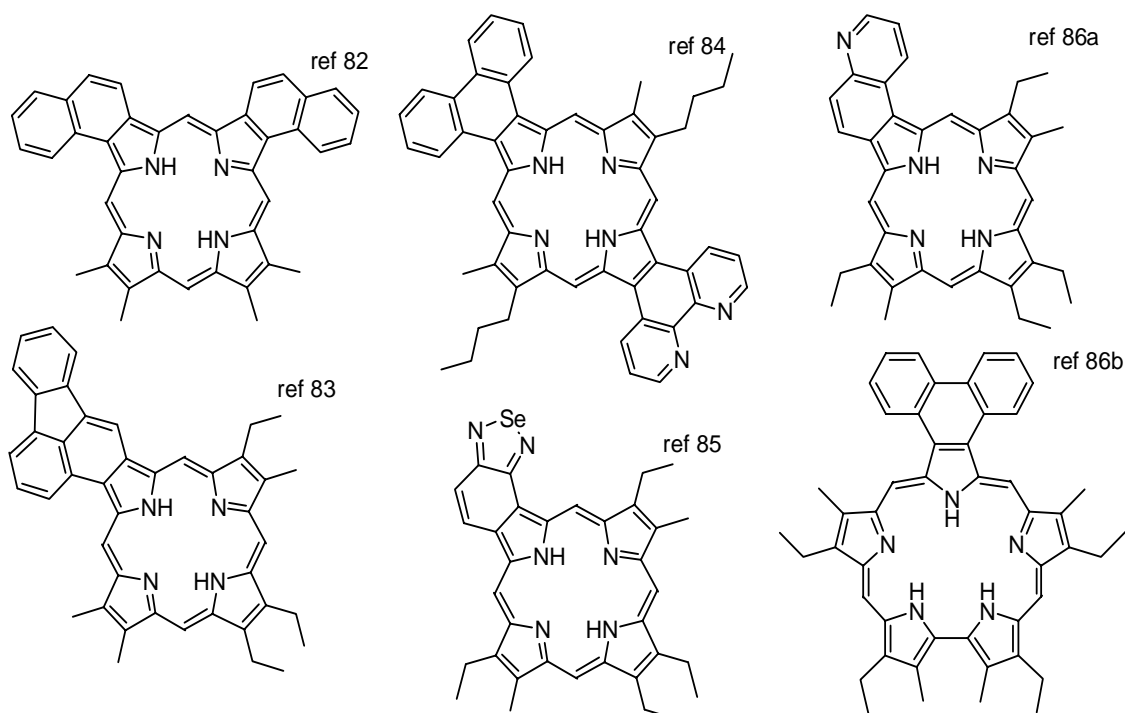
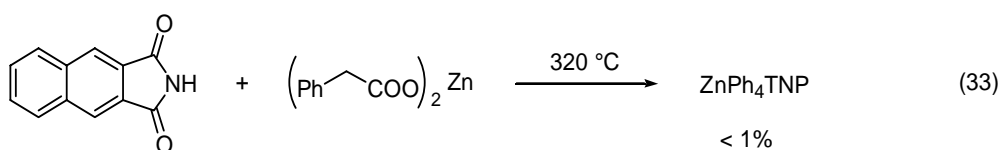
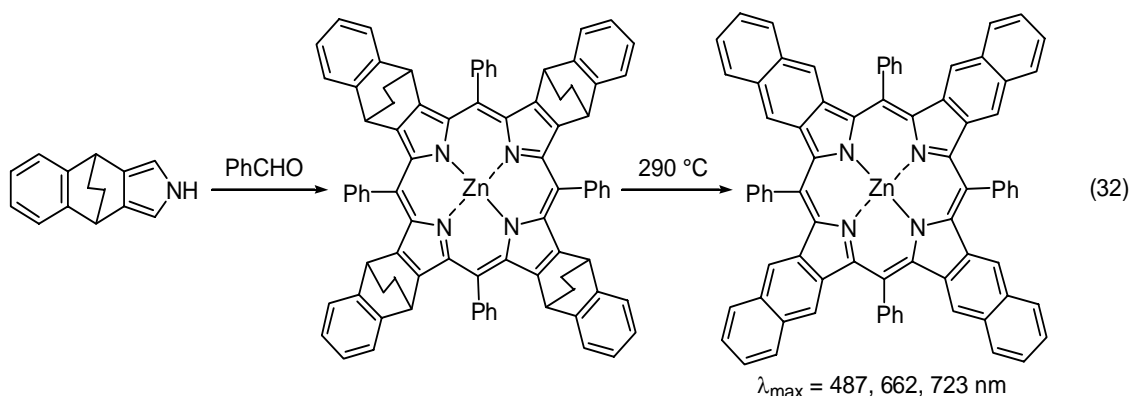
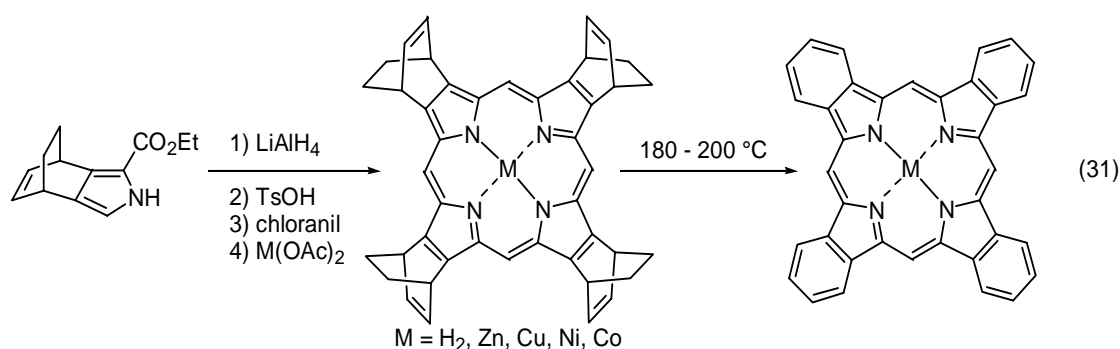


Figure 6 Porphyrins Fused with Exocyclic Rings via the BZ reaction

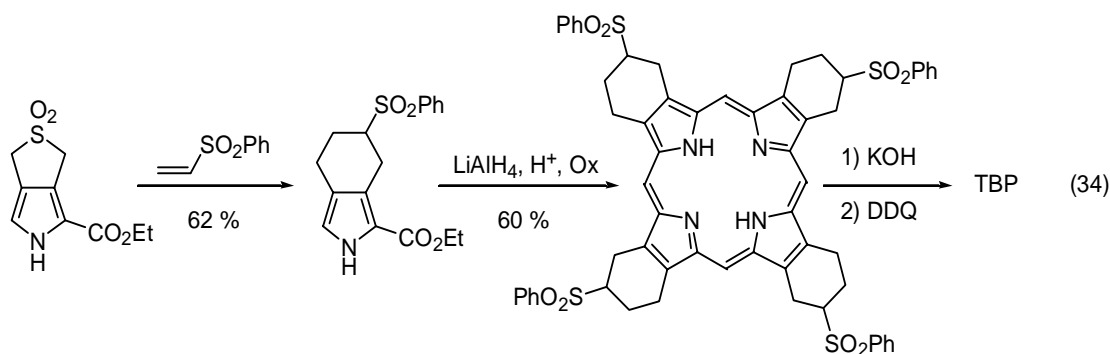
Extension of TBP synthesis in eq 31 leads to the synthesis of [2,3]naphthoporphyrins⁸⁹ and [2,3]anthraporphyrins⁹⁰ as shown in eq 32. The requisite pyrroles are prepared by the BZ reaction of the appropriate α,β -unsaturated sulfones which are prepared via sulfonylation of cyclic alkenes. The

ethoxycarbonyl groups are removed by heating with KOH in ethylene glycol at 180 °C to give α -free pyrroles, which give the corresponding bicyclo fused *meso*-tetraphenylporphyrins by the reaction with benzaldehyde in the presence of acid and subsequent oxidation with DDQ. Subsequent retro Diels-Alder reaction of these porphyrins gives *meso*-tetraphenyltetranaphtho[2,3]porphyrin (Ph₄TNP; Zn complex λ_{\max} 487 and 723 nm) and *meso*-tetraphenyltetraanthra[2,3]porphyrin (Ph₄TAnP, Zn Complex: λ_{\max} 496 and 803 nm). The old approach to them,⁹¹ based on a high temperature condensation of [2,3]naphthalenedicarboxyimide, or [2,3]anthracenedicarboxyimide with arylacetic acids, was of low practicability due to the required severe reaction conditions, low yields, and laborious purification (eq 33). The absorption of ZnPh₄TNP (698 nm), and ZnPh₄TAnP (770 nm) prepared by the old procedure are reported in the literature.⁹² Compared to the Q band of 723 nm and 803 nm of these compounds, the old reported values are blue shifted by 30 nm. This means that the porphyrin prepared by old method of eq 33 is not a target porphyrin, but a mixture of ZnPh_nTNP (n = 2-4), and it is difficult to separate a pure sample from the mixture.⁹¹ As Ph₄TAnP is very sensitive to O₂, it is very difficult to get pure one by old methods.

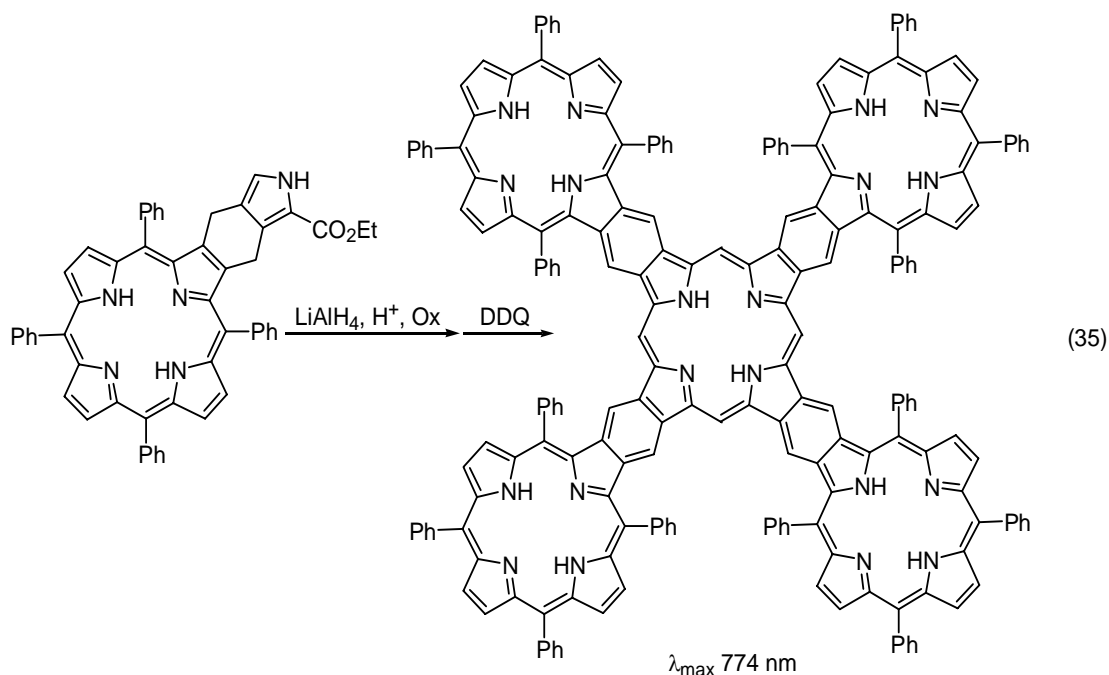


The oxidation of cyclohexene or cyclohexane rings is also useful for the preparation of benzo and naphthoporphyrins. For example, TBP is prepared by the process of eq 34, where pyrrole-fused 3-sulfolene is prepared by the BZ reaction followed by the Diels-Alder reaction with vinylphenylsulfone, porphyrin synthesis, elimination of sulfonyl groups and oxidative aromatization of fused-cyclohexene

rings.⁹³ Recently, more efficient and reliable method is reported. The BZ reaction using 1-phenylsulfonyl-1,4-cyclohexadiene gives 4,7-dihydroisoidole, which is converted into Ar₄TBP by the Linsey method and followed by oxidation.⁹⁴



The Diels-Alder adduct between pyrrole fused with sulfolene and *meso*-tetraphenylporphyrin (TPP) is further converted into tetrabenzoporphyrin fused with TPP as shown in eq 35 via oxidative aromatization of a precursor.⁹⁵



The strategy oxidative aromatization of a precursor has been used for synthesis of substituted Ar₄TBP⁹⁶ and Ar₄TNP^{97,98} derivatives, where the requisite starting pyrroles are prepared by the BZ reaction of α,β -unsaturated sulfines (eq 36 and 37). The absorption spectra of these samples are in good agreement with those of samples prepared based on the retro Diels-Alder reaction. Pd complexes of Ar₄TNP exhibit strong absorption at 710-720 nm ($\epsilon = \text{ca } 200,000 \text{ M}^{-1} \text{ cm}^{-1}$) and phosphoresce at room temperature with moderate quantum yields ($\psi = 2\text{-}3\%$), λ_{\max} 900-1000 nm.^{97,98} *meso*-Unsubstituted TBP and TNP with functional groups at the benzene rings (Figure 7) are also prepared by the similar procedures.⁹⁹ Coordination of a heavy metal atom increases the rate of the intersystem crossing between singlet and triplet states of the metalloporphyrins, thereby enhancing the rate of radiative decay from the

triplet state. For these reasons, PdTBP and PtTBP are regarded as good candidates for near infrared (NIR) phosphorescence materials. They can be used for NIR electro phosphorescence (OLED)¹⁰⁰ fluorescent sensors in biological systems¹⁰¹ and other photonic device applications. Introduction of aryl groups at the *meso* positions induces the saddle type distortions to cause red-shifts in the optical spectra of porphyrins.

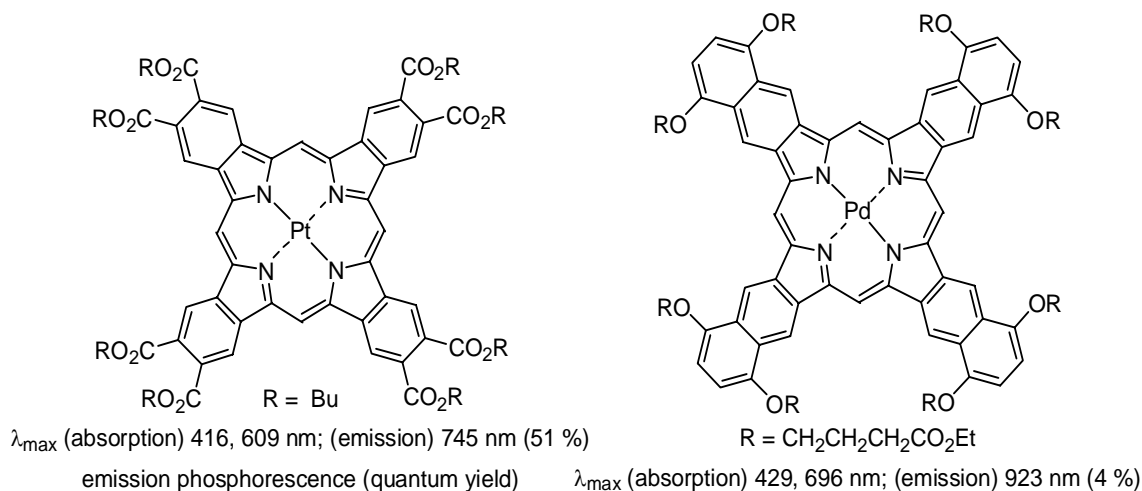
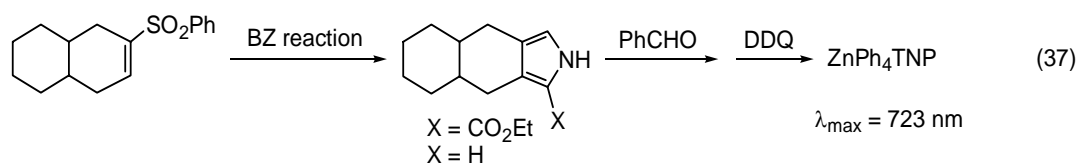
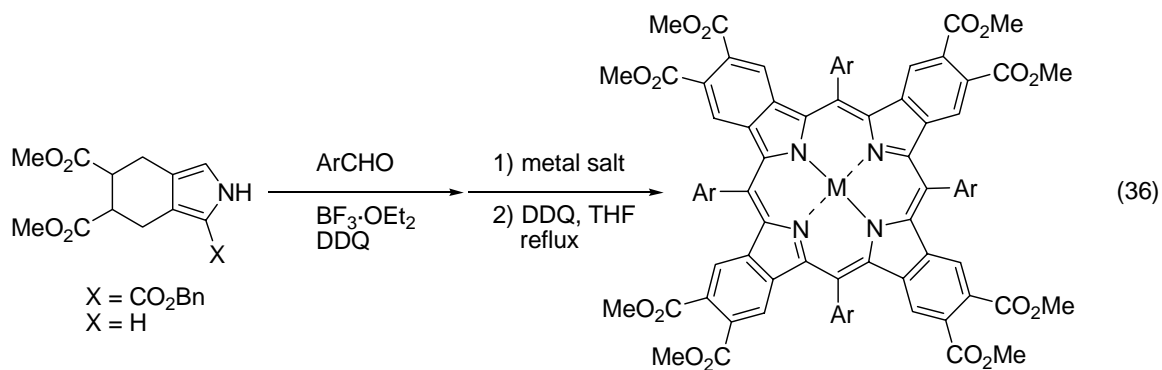
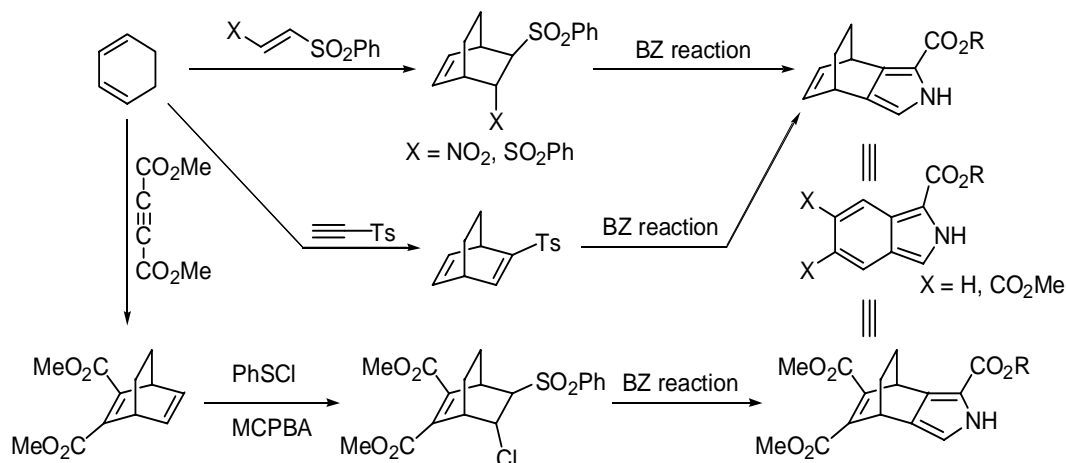


Figure 7 Phosphorescence of TBP and TNP

Thus, TBP and TNP derivatives can be prepared either by the retro Diels-Alder method or oxidative aromatization of precursors fused with cyclohexene units. If pure samples are required, the retro Diels-Alder route is definitively the method of choice. Namely, the insoluble materials are prepared in a highly pure state without purification steps, where byproduct is only ethylene. The drawback of retro Diels-Alder strategy is pointed to be difficult to get the BCOD fused pyrroles. The first synthesis of them was done via Diels-Alder reaction of 1,3-cyclohexadiene with β -(phenylsulfonyl)nitroethylene,⁸⁷ and later the process was improved by use of (*E*)-1,2-bis(phenylsulfonyl)ethylene followed by the BZ reaction.¹⁰² (*Z*)-1,2-Bis(phenylsulfonyl)ethylene works also effectively for this purpose. The Diels-alder reaction of sulfonylacetylene and subsequent BZ reaction is the simplest way to get the requisite pyrrole.¹⁰³

Combination of 1,3-cyclohexadienes with various dienophiles and sulfonylation affords various kinds of BCOD fused pyrroles, which are regarded as masked isoindoles as shown in Scheme 6.¹⁰⁴



Scheme 6 Synthesis BCOD Fused Pyrroles

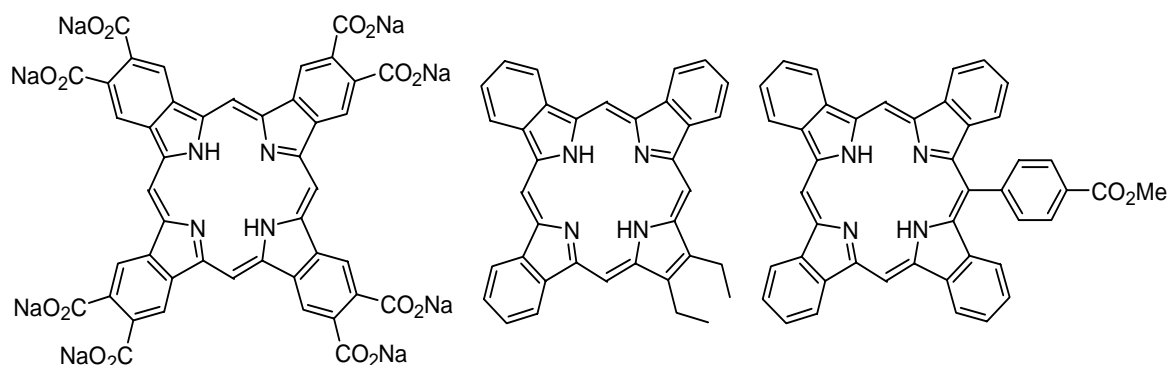


Figure 8 Benzoporphyrins Prepared by retro Diels-Alder Reaction

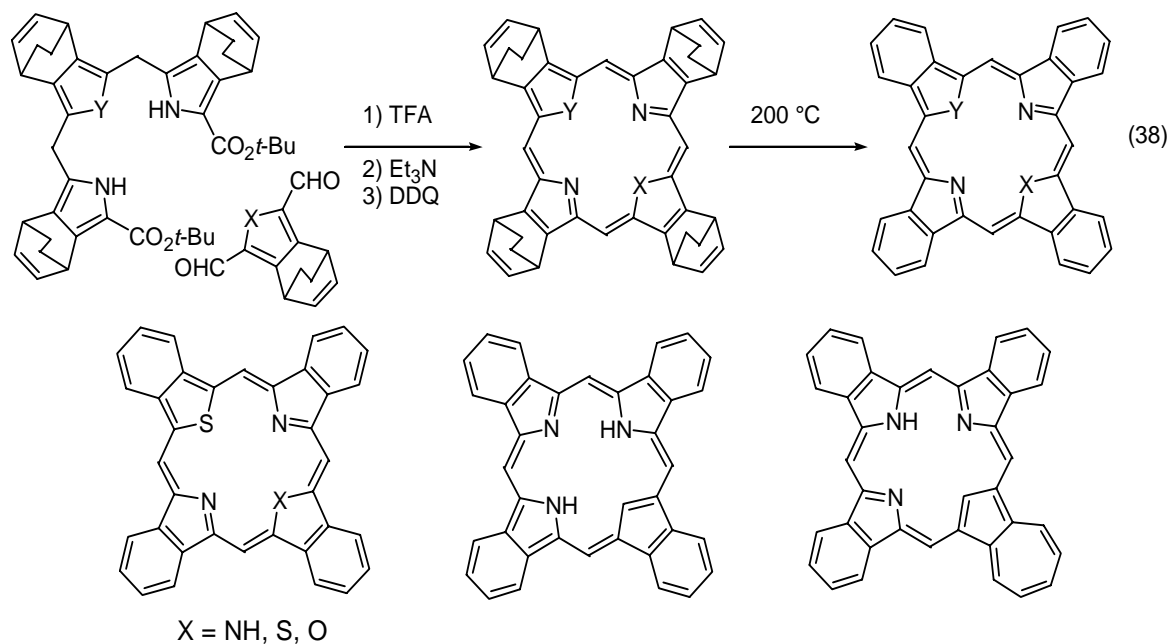


Figure 9 Core Modified TBP Prepared by retro Diels-Alder Reaction

Pyrroles fused with BCOD are used for synthesis of various types of benzoporphyrins such as water soluble BP,¹⁰⁴ monobenzoporphyrins,⁸⁸ dibenzoporphyrins,⁸⁸ tribenzoporphyrins,¹⁰⁵

meso-monoarylTBP,¹⁰⁶ and *meso*-diarylTBP.¹⁰⁷ A BCOD-fused tripyrrane and thiatripyrrane were synthesized as versatile reagents for the preparation of π -expanded heteroporphyrins. The reaction of the tripyrrane with diformylheterocycles afforded the corresponding heteroporphyrins, which were easily converted into tetrabenzoheteroporphyrins by retro Diels-Alder reaction.^{105,108}

The condensation of BCOD-fused tripyrrane with appropriate pyrrole dialdehydes and the subsequent retro Diels-Alder reaction affords acenaphthotribenzoporphyrin and fluoranthene-fused TBP.¹⁰⁹ The absorptions of these new porphyrins are very intense at both Soret and Q bands as shown in Figure 10, where the bold lines show the UV-Vis spectra after heating of BCOD-fused porphyrins. The final products are interesting, because their absorption covers wide range of wavelength, which are good candidates as dyes for solar cells.

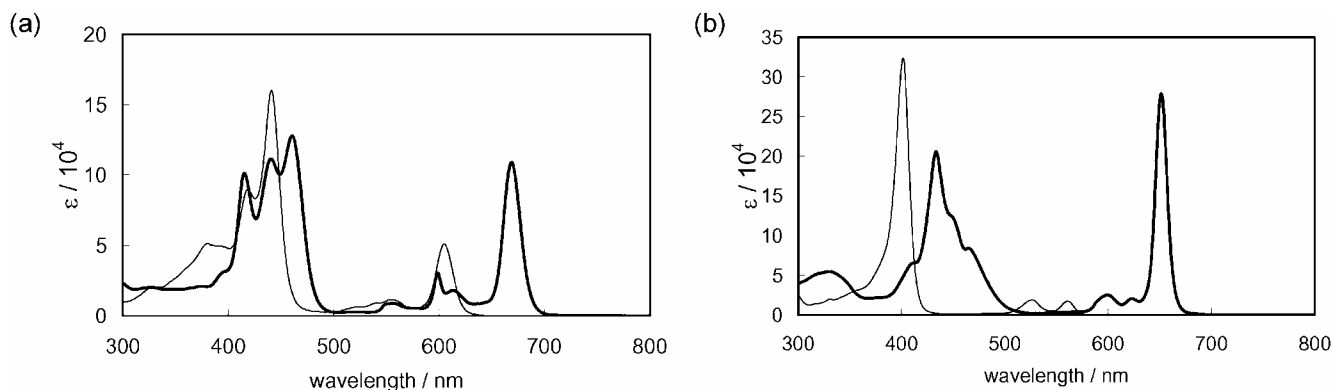
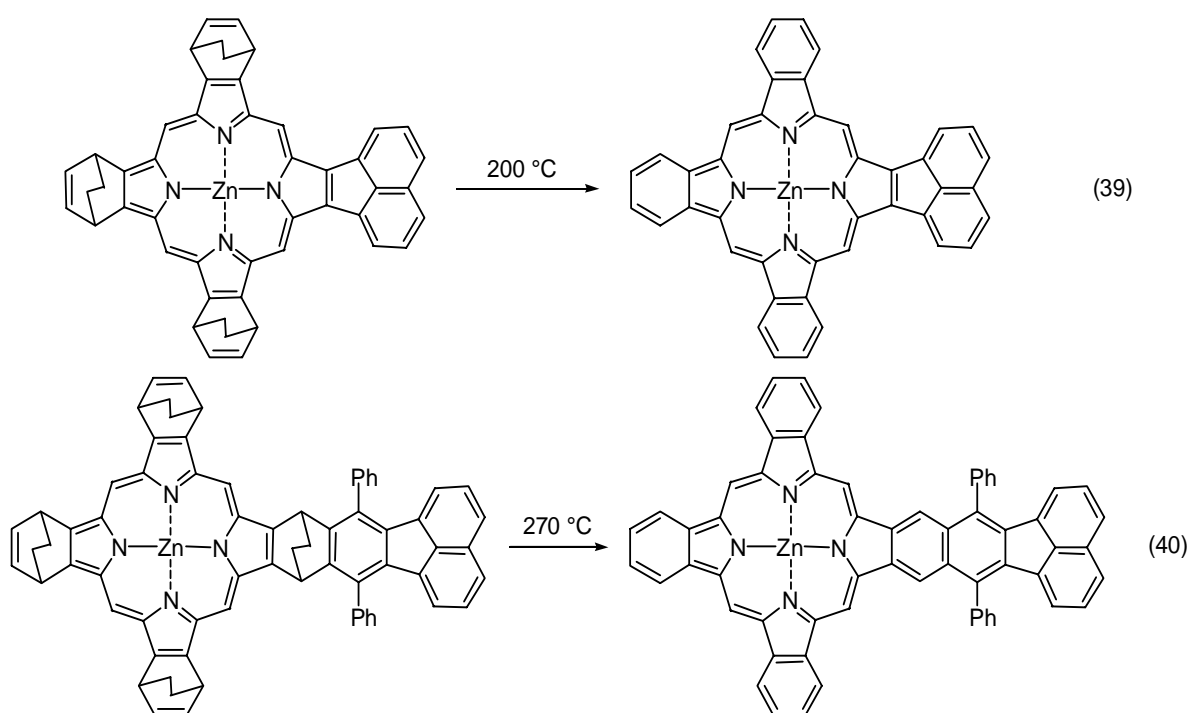


Figure 10 (a) Acenaphthotribenzoporphyrin (bold line) (b) Fluoranthene-fused TBP (bold line)

Sapphyrins are typical expanded porphyrins, whose absorption band at 453 nm is extremely narrow and strong. Sapphyrins fused with BCOD rings show absorption at 453-456 nm, which are converted into monobenzosapphyrin, dibenzosapphyrin, tribenzosapphyrin, and pentabenzosapphyrin by heating at 200

°C, the Soret bands at 453 nm are red-shifted by about 10 nm (monobenzo), 20 nm (dibenzo), 30 nm (tribenzo) and 50 nm (pentabenzo), respectively, depending on the numbers of fused benzene rings.¹¹⁰

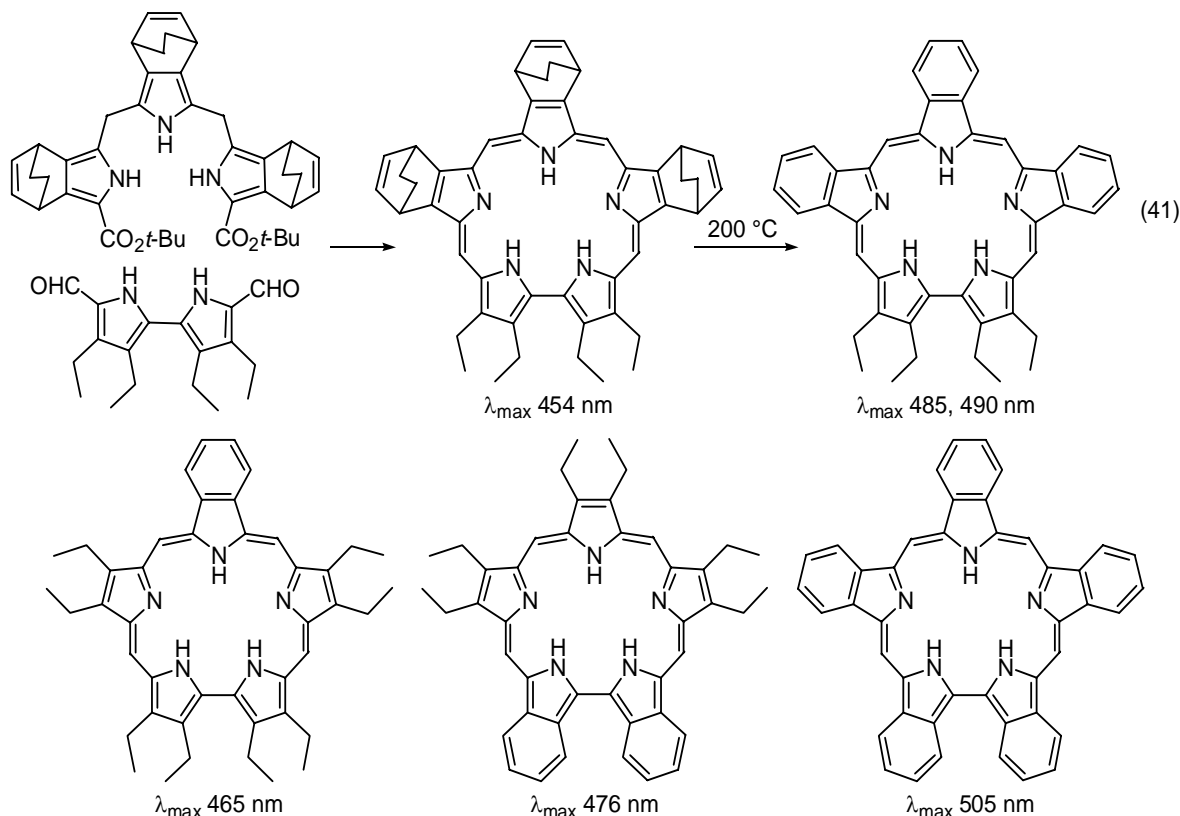
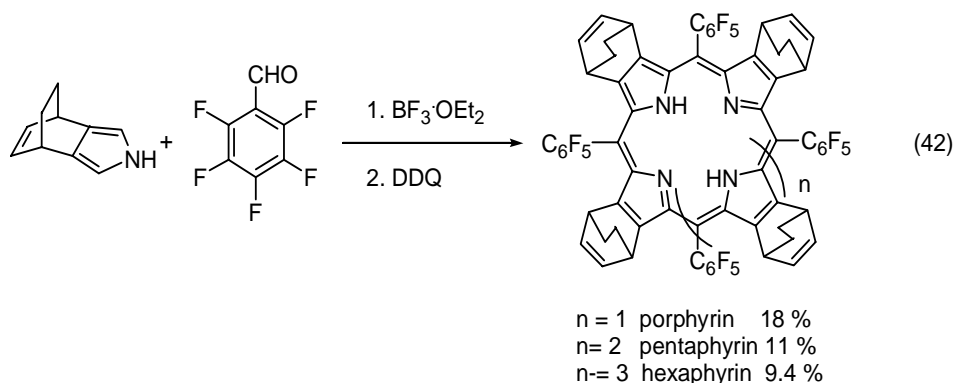


Figure 11 Benzosapphyrins Prepared by retro Diels-Alder Reaction

Osuka and his coworkers have developed the preparation of *meso*-aryl expanded porphyrins by the reaction of pentafluorobenzaldehyde with pyrrole by the conditions using $\text{BF}_3 \cdot \text{OEt}_2$ and DDQ. This strategy is applied to the reaction of BCOD-fused pyrrole to give porphyrin, pentaphyrin, and hexaphyrin fused with BCOD. Heating them gives the corresponding benzoderivatives. Interestingly, a doubly *N*-fused benzohexaphyrin is formed in the case of BCOD-fused hexaphyrin, which is further rearranged to a fluorescent macro cycle upon DDQ oxidation (see compounds in Figure 12).¹¹¹



Porphyrin dimers or further oligomers with highly ordered molecular systems are subject to extensive studies of electron and energy transfer between porphyrin units.¹¹² Porphyrins are linked with suitable

spacers such as aromatic rings or ethylene units, which is well documented by the excellent reviews.¹¹² The BZ reaction provides a novel strategy for construction of porphyrin oligomers, which are difficult to prepare by other methods. For example, *meso*-unsubstituted porphyrin dimers linked with 1,3- and 1,4-phenylenes are prepared from the corresponding phenylenedipyrroles by double [3 + 1] MacDonald condensation. The requisite dipyrroles are readily prepared by the BZ reaction starting from aromatic aldehydes as presented in eq 43. Acid catalyzed condensation of tripyrranes with pyrrole-2,5-dicarbaldehydes, followed by oxidation affords porphyrin dimers.¹¹³ Equation 44 shows synthesis of directly linked β,β' -porphyrin dimer, where the requisite β,β' -linked pyrrole dimer is prepared via the BZ reaction. The subsequent [2 + 2] MacDonald condensation gives the desired pyrrole dimers in 10% yield.¹¹⁴ Such porphyrin dimers are alternatively prepared by the Suzuki coupling starting from β -bromo porphyrins.¹¹⁵ Some β -substituted porphyrins show axial chirality and each stereoisomer can be separated.¹¹⁶

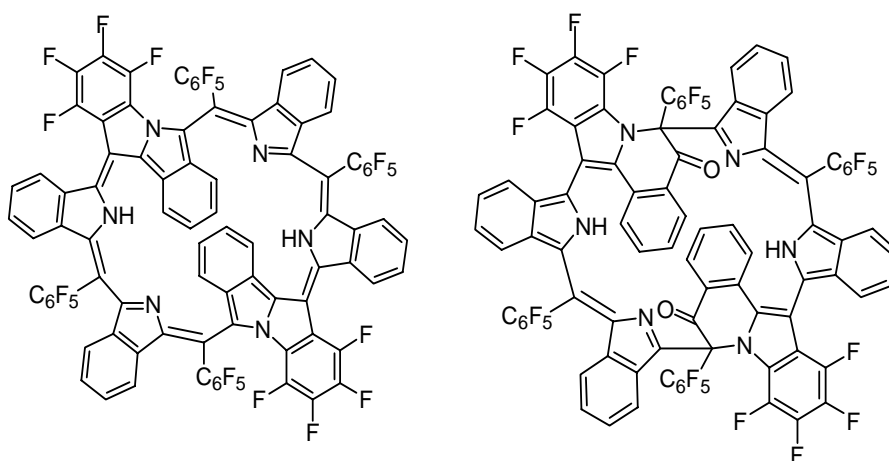
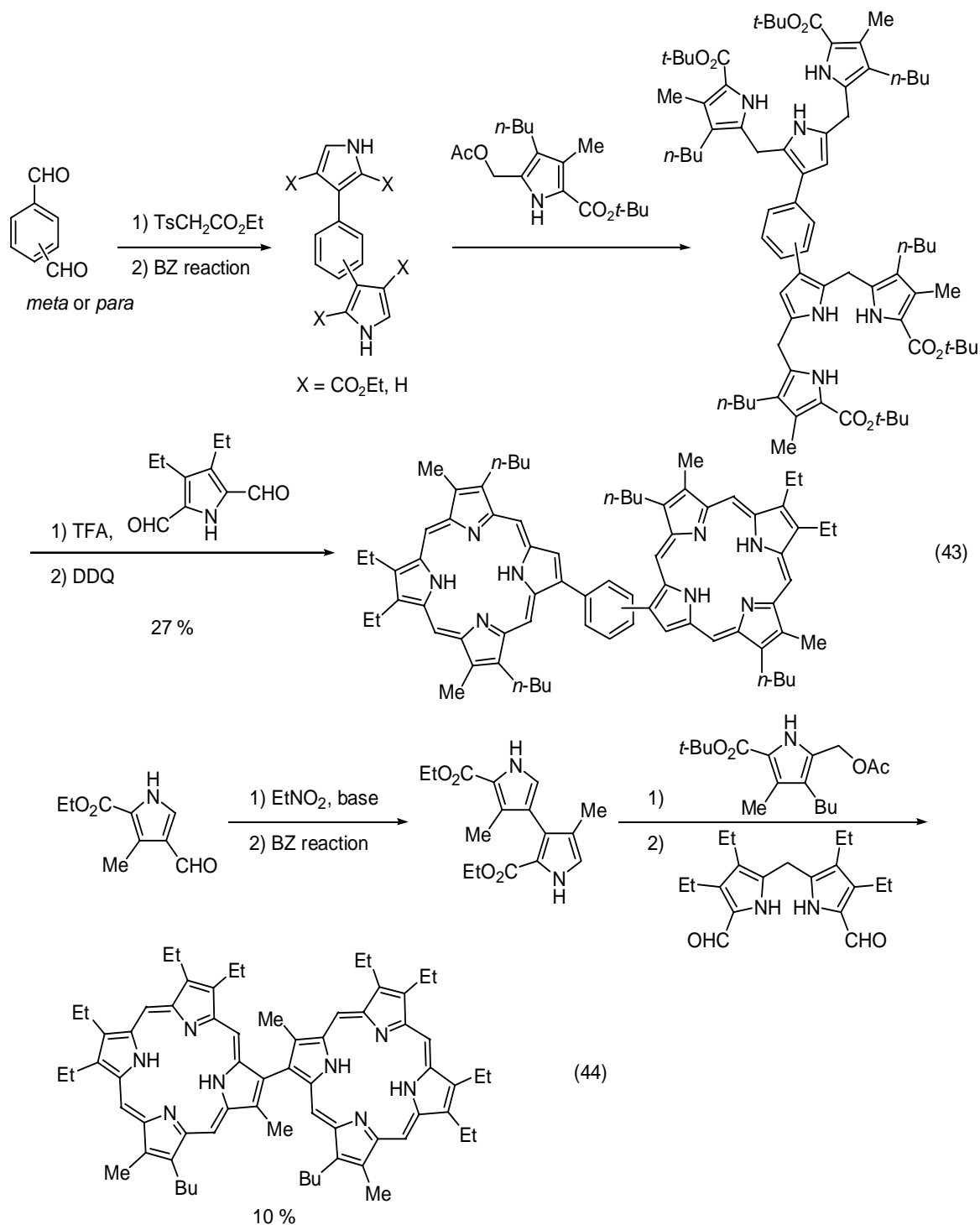


Figure 12 Rearranged Products of Hexabenzohexaphyrins

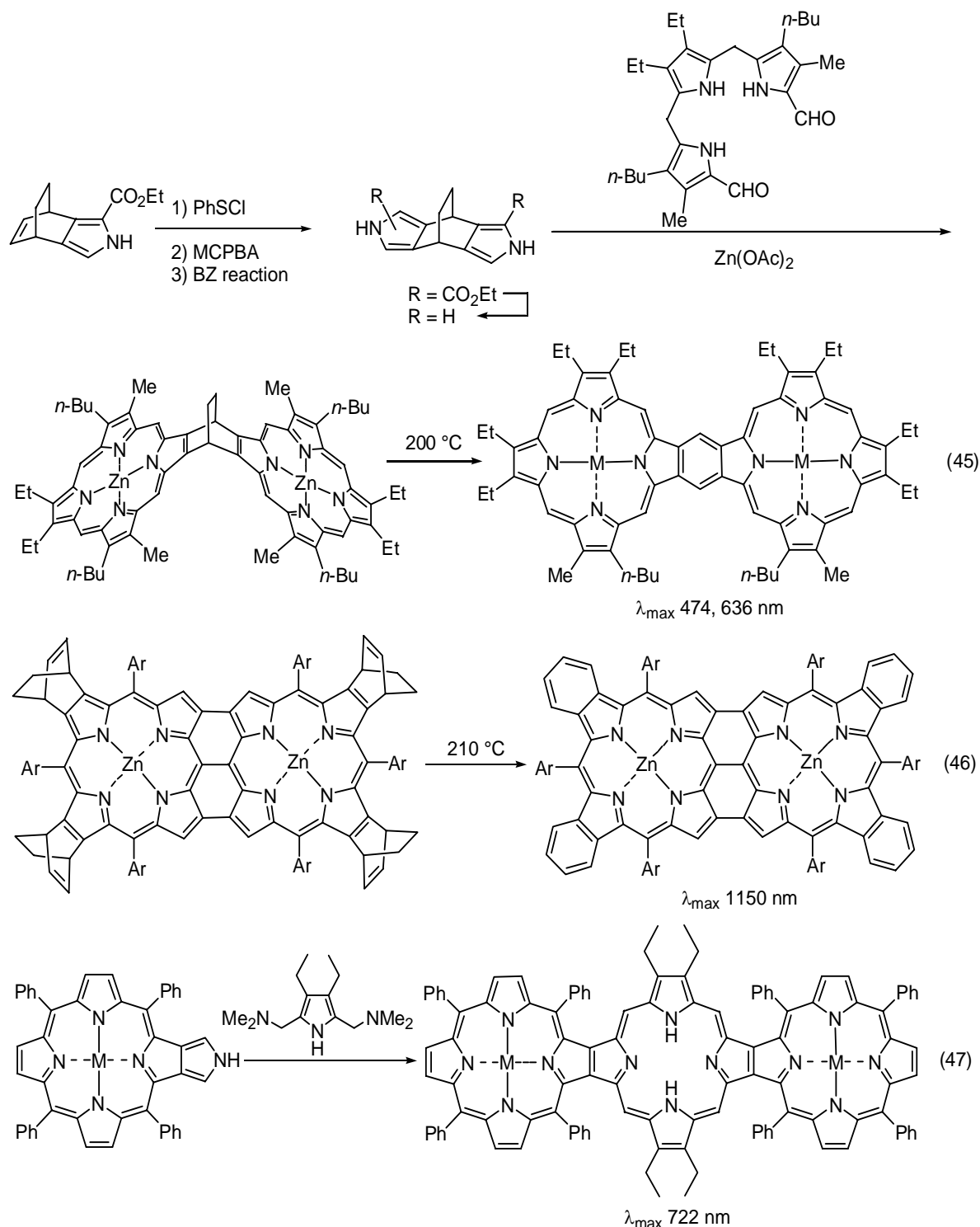
Highly conjugated porphyrins are important as optical and electronic materials. For example, they are good materials for non-linear optics, semiconductors, or sensitizers of photo dynamic therapy of cancer. In general, π -conjugated molecules are difficult to be purified due to the low solubility. This difficulty is resolved by using the BCOD fused porphyrins which are soluble in organic solvents. Thus, they are purified by column chromatography or recrystallization followed by the thermal reaction (retro Diels Alder reaction). Pyrrole fused with BCOD ring is further converted into bispyrrole fused with BCOD via sulfonylation of the double bond and the BZ reaction. The gable type of porphyrin dimer linked with a rigid BCOD ring is prepared from this bispyrrole by the inverse type [3 + 1] porphyrin synthesis as shown in eq 45. Heating a soluble gable bis-porphyrin at 200 °C affords an insoluble conjugated planar bis-porphyrin. The retro Diels-Alder strategy is useful to prepare insoluble planar conjugated systems. Zn complex of gable porphyrin shows absorptions at 399 and 415 nm as split Soret band, weak Q bands at 533 and 575 nm. Zn complex of planar dimer shows absorptions at 474 nm (Soret band) and intense Q

band at 636 nm in CHCl_3 containing 1% pyridine. Such dramatic change is caused by heating, which is the advantage of this process.¹¹⁷



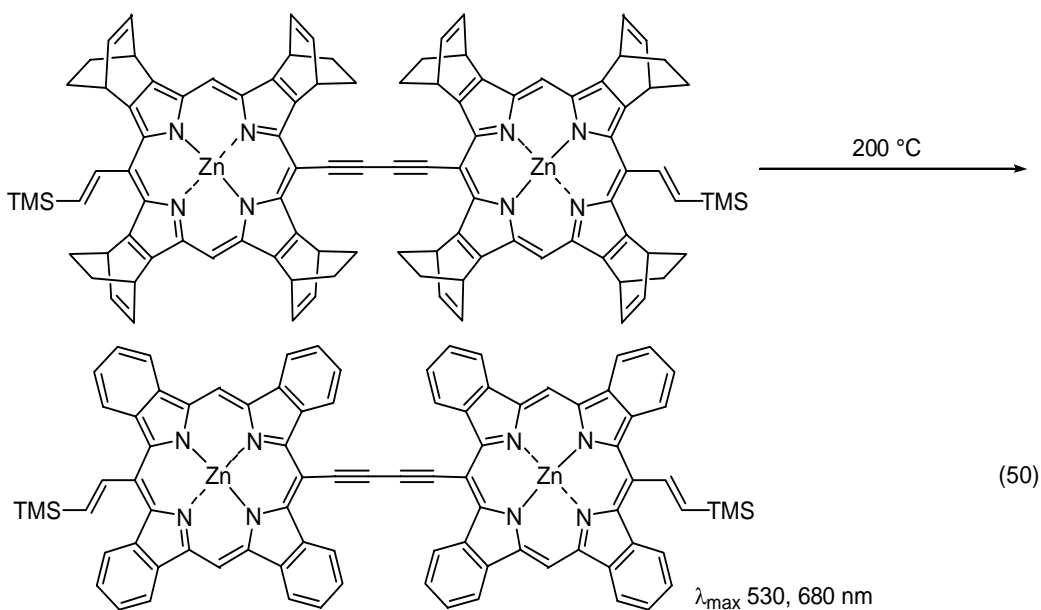
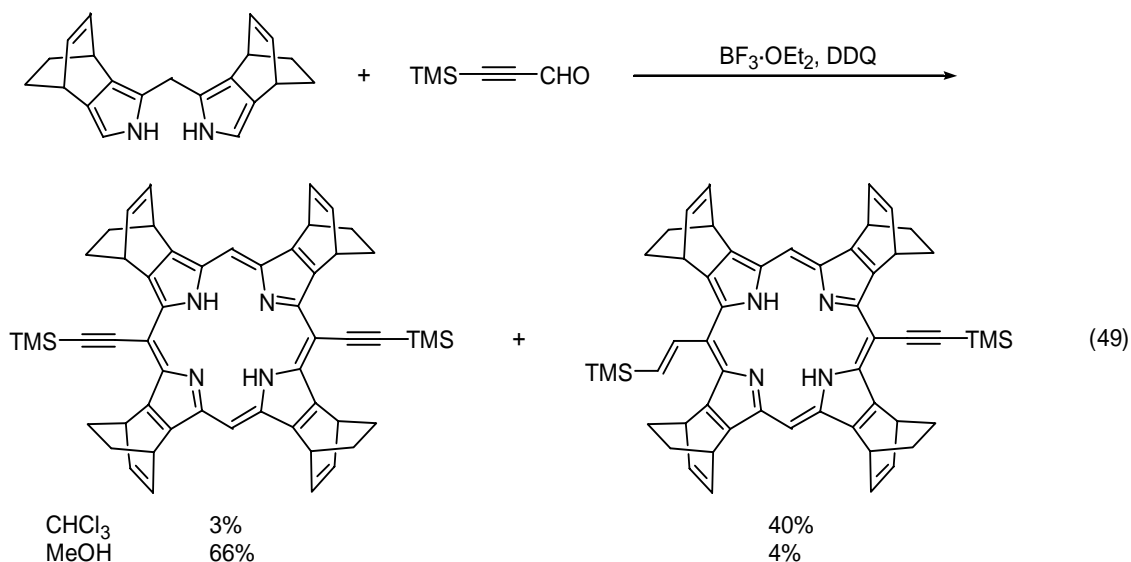
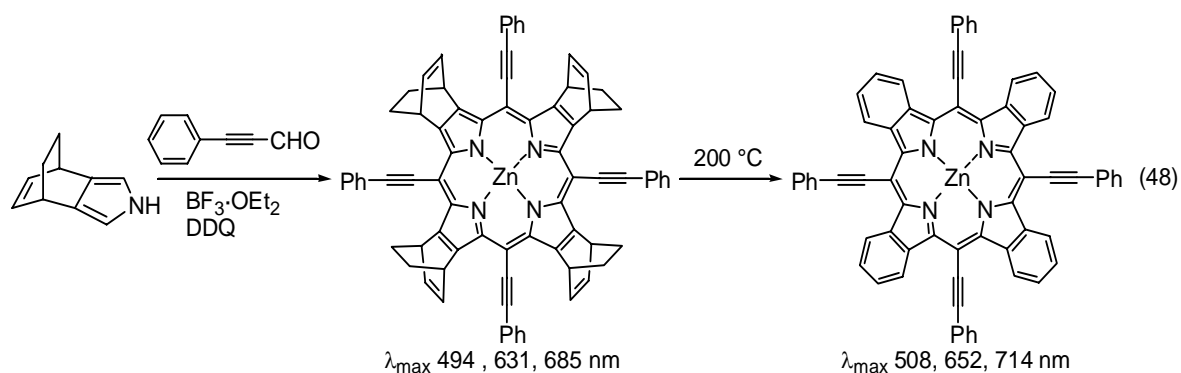
Osuka group has developed *meso-meso*, $\beta\text{-}\beta$, $\beta\text{-}\beta$ triply linked porphyrin arrays, which exhibit extremely red-shifted absorption spectra and promise useful opt electronic applications. It is expected that a *meso-meso*, $\beta\text{-}\beta$, $\beta\text{-}\beta$ triply linked dibenzoporphyrin dimer has enlarged π -electronic network. The final compound exhibits a large two-photon absorption cross section (15,400 GM).¹¹⁸

Another synthetic approach to directly fused porphyrin trimers is demonstrated by Smith, where fused pyrroloporphyrin (prepared by the BZ reaction of β -nitroporphyrin) is condensed with 3,4-diethyl-2,5-di(amionomethyl)pyrrole. This highly conjugated porphyrin absorbs a light at 468 and 722 nm.¹¹⁹



The red-shifted electronic absorption spectra of *meso*-ethynylporphyrins, which result from efficient porphyrin-acetylene conjugation, make them for applications in non-linear optics and light harvesting.¹²⁰ So many *meso*-alkynylporphyrins and their oligomers have been prepared, and their optical properties

have been studied. For example, such porphyrins are useful as optical limiters, which are transparent at normal light intensities, but opaque to very bright light. They can be used to protect sensors from intense light sources such as lasers. So, *meso*-tetrakis(phenylethynyl)porphyrin is expected to have a small HOMO-LUMO energy gap. It is readily prepared by the condensation of BCOD fused pyrrole with propargylaldehyde and the subsequent retro Diels-Alder reaction.¹²¹



5-Alkenyl-15-alkynyl porphyrin and 5,15-dialkynylporphyrin are selectively prepared by the reaction of [2+2] acid-catalyzed condensation of BCOD fused dipyrromethane with TMS propynal depending on solvents. Such unsymmetrical porphyrin is formed only in the presence of BCOD ring and TMS groups in the reactants. This porphyrin is converted to butadiyne dimer by selective desilylation of the alkynyl TMS. The retro Diels-Alder reaction affords butadiyne-linked benzoporphyrin dimer, whose absorption λ_{\max} is 530 and 680 nm.¹²²

CHAPTER 3 SYNTHESIS OF POLYPYRROLES

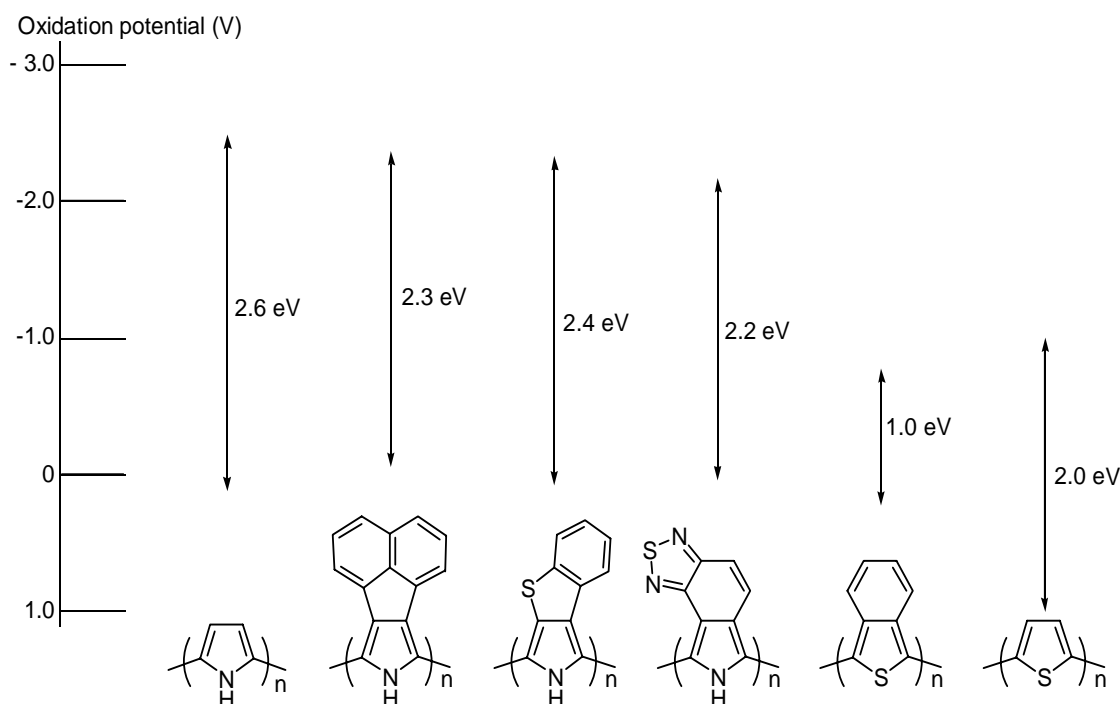


Figure 13 Energy Levels of Conducting Polymers

Conductive polymers derived from heteroaromatics such as pyrroles, thiophenes or furans comprise a huge class of materials that have received much attention due to their interesting electrical properties. Among them, polypyrroles are exceptionally versatile, they are readily obtained by anodic oxidation or chemical oxidation of α -free pyrroles.⁸ The BZ reaction affords α -free pyrroles with various substituents at the 3- and/or 4-positions, which are important starting materials for polypyrroles. For example, the pyrroles prepared by the BZ reaction of polycyclic aromatic nitro compounds and subsequent deethoxycarbonylation (Scheme 3) afford interesting polypyrroles fused with aromatic rings by anodic oxidation or chemical oxidation.⁴³ Band gaps of these polypyrroles are considerably lower than those of unsubstituted polypyrroles or alkyl substituted polypyrroles. Furthermore, band gaps and HOMO-LUMO energy levels are finely controlled by the change of fused aromatic rings and substituents of aromatic rings. Oxidation potentials (Ag/AgNO₃ measured by CV) and band gaps (estimated by absorption edge) are summarized in Figure 13. Polypyrrole derived from acenaphtho[1,2-c]pyrrole shows a good

conductivity, 4.1 S/cm, when it is polymerized at a potential of 2V in the presence of Bu_4NPF_6 .⁴³ Fused aromatic rings helps π - π stacking of between polymers to increase the conductivity of this polymer. In general the conductivity of 3,4-disubstituted polypyrroles is low (10^{-2} S/cm), compared to that of polypyrrole itself.⁸ Long alkyl chains can be introduced at the aromatic rings which increases the solubility of polymer without loss of its conductivity.¹²³ This is the merits of this material for developing of solution processable organic semiconductor devices.

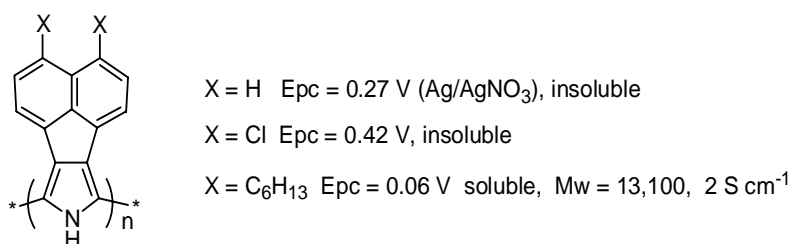
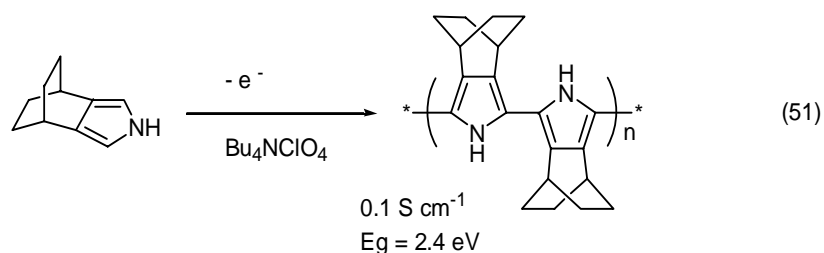


Figure 14 Acenaphthopyrrole and their Properties

Polypyrrole fused with bicyclo[2.2.2]octane (BCO) provides a new material that possesses a raised HOMO band, extended conjugation and a rigid porous structure. Electrochemical properties of pyrrole fused with bicyclic ring are compared with those of pyrrole itself and 3,4-diethylpyrrole to show the reversible oxidation-reduction peaks at lower potentials ($E_{pa} = -0.36$ V, versus Ag/AgNO₃) of this pyrrole. This suggests that the counter ion ClO_4^- moves easily in the polypyrroles fused with rigid framework. The rigid framework of bicyclic units helps to fix the anti-periplanar conformation of the polypyrroles to extend the effective conjugation. Thus, the polypyrrole fused with bicyclic rings shows the low band gap (E_g) and high conductivity compared to those of polymer derived from 3,4-diethylpyrrole.¹²⁴ So, such polypyrroles are interesting materials for chemical sensors or molecular wires. In fact, this idea is realized in electro analytical method of polypyrrole coated mercury film electrode for anode stripping voltammetry (ASV) analysis of cadmium and lead. ASV is the convenient method for the analysis of heavy metals in environmental samples. Electrodes coated with polymer films that allow passage of the analytes to the electrode while restricting the access of surface-active compounds yield improved signal quality. Poly (4,9-dihydro-*o*-benzenonaphtho[2,3-*c*]pyrrole) is the best choice as polymer film for ASV, where the rigid three dimensional structure of this polymer helps to move heavy metal ions.¹²⁵ The requisite pyrrole is prepared by the Diels-Alder reaction of anthracene with β -sulfonylnitroethylene followed by the BZ reaction. Komatsu and his coworkers have developed a technique to stabilize the cationic species of π -conjugated systems by annelation with BCO units including oligothiophenes and acenes.¹²⁶ The BZ reaction is a good method for providing pyrrole derivatives fused with BCO units.



Hydrogen bonding is also effective to keep the rigid structure of pyrrole oligomers as demonstrated in dimers containing pyrrolo[3,4-*e*][2,1,3]benzothiadiazole units as shown in Figure 15.¹²⁷ This compound shows narrow HOMO-LUMO gap, and strong hydrogen bonding is evidenced by NMR chemical shifts. The requisite pyrroles are readily prepared by the BZ reaction as shown in eq 20. The dimer of 3-ethoxycarbonyl pyrrole shows a similar coplanar structure through hydrogen bonding, and it shows a strong blue emission due to the rigid structure.¹²⁸ Such pyrrole dimer is useful as an organic light emitting diode of a blue color emitter.

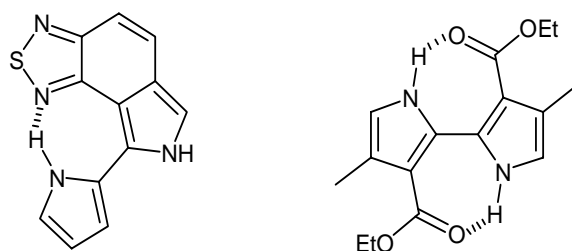
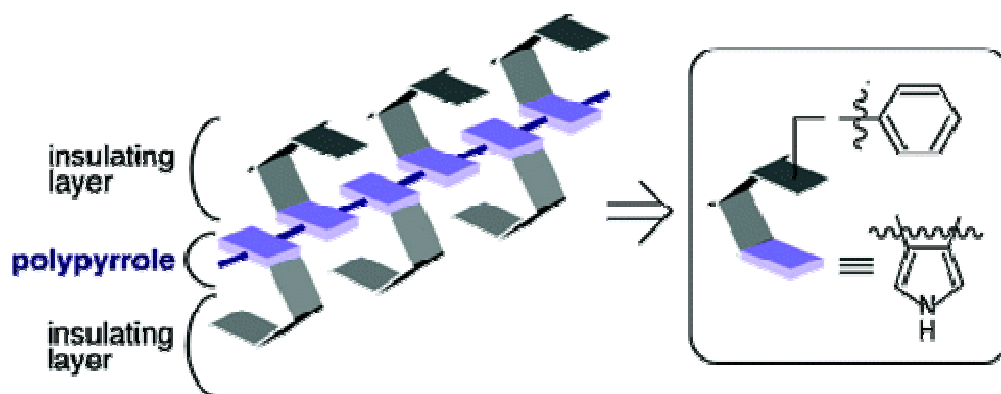
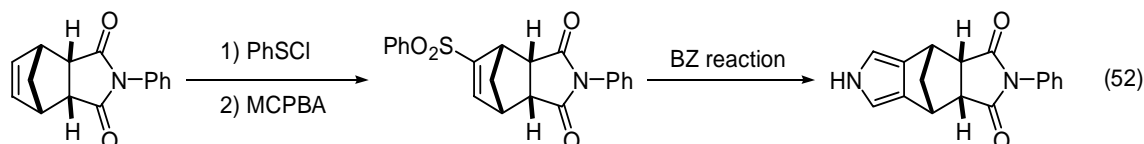


Figure 15 Rigid Pyrrole Dimers Containing Hydrogen Bonding

Swager and his coworkers have developed isolated molecular wires by electropolymerization of bicyclo[2.2.1]heptane-fused pyrrole, where a phenyl group is rigidly placed proximate the pyrrole fragment. Oxidative polymerization of this pyrrole affords highly conductive polypyrrole. The rigid molecular scaffold limits cross communication between adjacent conducting strands to allow for superior sensory properties (Scheme 7).¹²⁹



Scheme 7^{129b}

CHAPTER 4 SYNTHESIS OF BORON DIPYRROMETHENE DYES

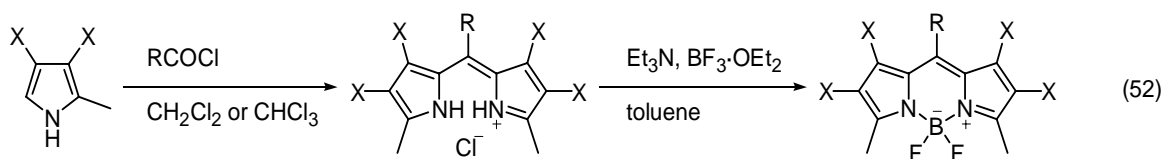


Table 1 Optical Properties of BDP Dyes

X, X =	R =	λ_{\max} (nm) ^a	$\log \epsilon^a$	Stokes Shifts (nm) ^b	Φ^c
	-Me	540	4.83	13	0.62
	- <i>n</i> -C ₅ H ₁₁	529	4.86	12	0.85
	-Me	530	4.89	11	0.77
	-Et	529	4.87	10	0.78
	- <i>n</i> -C ₃ H ₇	530	4.78	12	0.80
	- <i>n</i> -C ₅ H ₁₁	529	4.82	10	0.79
	- <i>n</i> -C ₁₁ H ₂₃	529	4.91	12	0.79
		534	4.85	19	0.62
	-Me	526	4.87	12	0.73
	-Me	603	5.19	6	0.57 (551), 0.28 (596)
	-Et	601	5.16	7	0.08 (551), 0.33 (596)
	- <i>n</i> -C ₃ H ₇	602	5.12	6	0.36 (595)
	- <i>n</i> -C ₅ H ₁₁	601	5.22	9	0.62 (550), 0.32 (595)
	- <i>n</i> -C ₁₁ H ₂₃	600	5.12	9	0.32 (595)
		606	5.13	10	0.26 (600)

^a Solvent in CHCl₃ ^b Solvent in CH₂Cl₂^c Solvent in EtOH; reference: fluorescein in EtOH (0.97) Ex/Em: 499/518

Boron dipyrromethene (BDP) dyes are highly fluorescent materials and have been extensively used in various fields of science. They are important for laser dyes, molecular probes for biochemical study, fluorescent sensors, or various optoelectronic devices. As a good review is available, the details of this topic should be referred to it.¹³⁰ Pyrroles obtained by the BZ reaction provide ideal starting materials for the preparation of BDP dyes. Namely, the ester group at the 2-position is reduced to hydroxymethyl or methyl with LiAlH₄ at 0 °C or room temperature, respectively. The groups at the β -positions are freely changed as discussed in the chapter 1, and α -free pyrroles are converted into BDP-BF₂ complexes by the reaction with acid chlorides or aldehydes followed by treatment with BF₃·Et₂O. A new class of BDP dyes fused with rigid bicyclic rings and benzoderivatives are prepared by the method based on the BZ reaction and the retro Diels Alder reaction of BCOD fused pyrroles.¹³¹ As shown in Table 1, very sharp and strong absorptions of BDP-BF₂ complexes fused with BCOD rings are observed at 530 nm, and they are

red-shifted at 600 nm after the retro Diels-Alder reaction. The strong sharp emissions and small Stokes shifts (ca 10 nm) are observed.¹³²

The color of BDP dyes is finely tuned by the choice of alkyl or fused rings of pyrroles as shown in Figure 16, where the absorption covers from 530 nm to 657 nm.

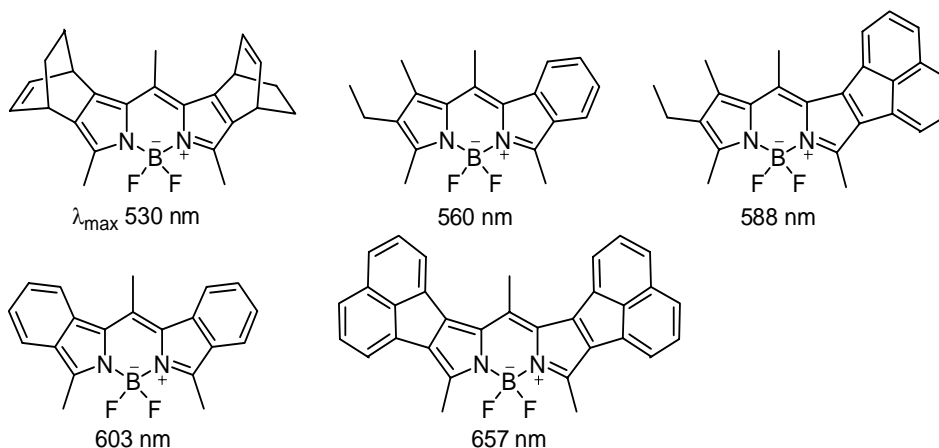


Figure 16 Control of Electronic Properties of BDP-dyes

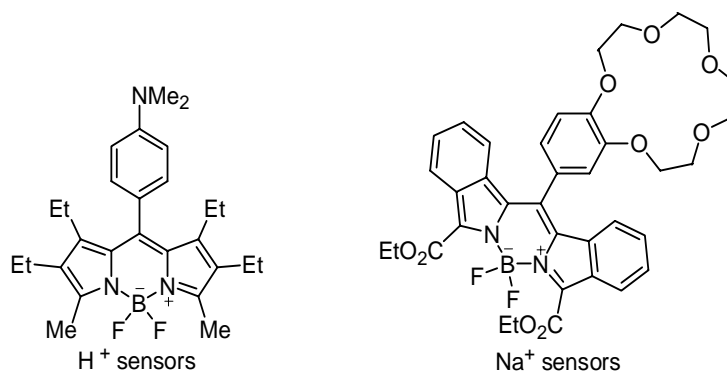


Figure 17 Fluorescent Sensor Using BDP dyes

Fluorometry is a frequently used method in biochemical and environmental analysis. Figure 17 presents a new fluorescent sensors based on BDP dyes. In polar solvents, the emission intensity of *meso*-4-dimethylaminophenylBDP-BF₂ is heavily quenched with the quantum yield of 0.012, which is due to the photo-induced electron transfer from the *meso*-4-dimethylaminophenyl donor to the BDP fluorophore. Gradually adding the H⁺ to the solution, the emission intensity increases significantly while the emission maxima centered at 540 nm remain unchanged. This compound provides a very sensitive fluorescent probe for H⁺ analysis.¹³³ To gain an analytically advantageous, amplified fluorescence signal from benzo crown-functionalized dyes upon analyte complexation, an exceptionally strong CT-process thus has to be installed in the uncomplexed molecule. Furthermore, for a straightforward application, it would be useful to have sensor molecules available that absorb and emit at rather long wavelengths, well within the visible or the near infrared spectral range. Benzo-fused BDP substituted *meso*-benzo crown ether is the choice of such sensors. In methanol, for instance, this charge transfer-type quenching process is manifested in decreased fluorescence lifetime and quantum yield (e.g. $\Phi_f = 0.05$), entailing

dramatically increased rate constants of non-radiative relaxation. Binding to Na^+ then leads to a switching “on” of the fluorescence, yielding e.g. $\Phi_f = 0.35$ for the complex.¹³⁴

Many other applications of BDP dyes are possible. Radical photopolymerization of methyl acrylate initiating by sensitization of BCO fused BDP is more active than that by other BDP dyes.¹³⁵ They are also effective as laser dyes, and their photostability are studied.¹³⁶ BDP dyes are useful as dopants in organic light emitting diode (OLED). For example, BDP- BF_2 complexes fused with rigid bicyclic rings are used as dopant in the OLED using Alq3 and aromatic amines to emit the very sharp green light (540 nm) with high efficiency.¹³⁷

CHAPTER 5 SOLUTION PROCESSABLE ORGANIC SEMICONDUCTORS

Electronic devices such as organic field effect transistors (OFETs) and thin film organic photovoltaic cells based on organic semiconductors are being developed to realize low-cost, large area electronic products on flexible substrates.^{9,138} An organic thin-film transistor is shown in Figure 18. The devices consist of deposited conduction (gate, source, and drain electrodes), an insulator (SiO_2 or plastics) and organic semiconductors. The thin-film transistor works as a switch, on/off states, when a bias is applied on the gate electrode, the gate is biased negatively or positively to induce hole or electron transport in organic semiconductor layers, respectively. Transporting hole or electron is p-channel or n-channel, respectively. In order to apply OFET for driving circuits in display applications, they need to exhibit high carrier output, good switching speed, and high contrast between the on and off states. They are related to several important parameters, namely, carrier mobility (cm^2/Vs), threshold voltage (V_{th}), and on/off current ratio. V_{th} is controlled by subtleties between the organic semiconductor-insulator interface that is not well understood. Mobility is the most important parameter for evaluation of OFET, and on/of ratio is the second important one. For display applications, a minimum mobility of $0.1 \text{ cm}^2/\text{Vs}$, and an on/off ratio of at least 10^3 are required.

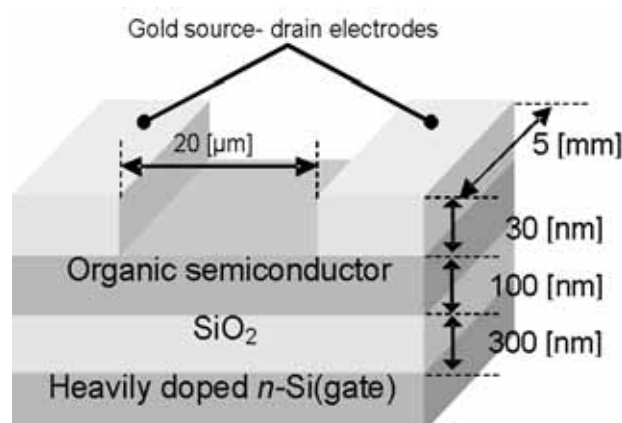
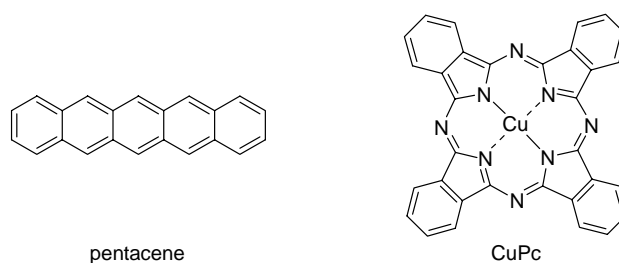


Figure 18 Illustration of top contact OFET device

Among many organic semiconductors, pentacene and phthalocyanines (CuPc) are one of the earliest applied small molecule organic semiconductors and still are subjected to intensive investigation. Device optimization leads to the very high mobility up to $3 \text{ cm}^2/\text{Vs}$ for vacuum-deposited OTFT of pentacene.^{9,138} CuPc is very attractive for application, because it is very stable toward to the light and air. However, the mobility of FET using CuPc (vacuum deposition) is as low as $0.02 \text{ cm}^2/\text{Vs}$,¹³⁹ and the mobility of single crystal CuPc is $1 \text{ cm}^2/\text{Vs}$.¹⁴⁰ CuPc seems to be the material of a choice for OFETs in displace application and organic solar cells applications. In both these applications, the large amount of light emitted (display) or absorbed (solar cell) would require a very stable semiconductor, and pentacene does not satisfy the requirement.



New organic semiconductors have been synthesized to improve carrier mobility, sensitivity and stability, some of them are listed in Figure 19, where mobility is presented.

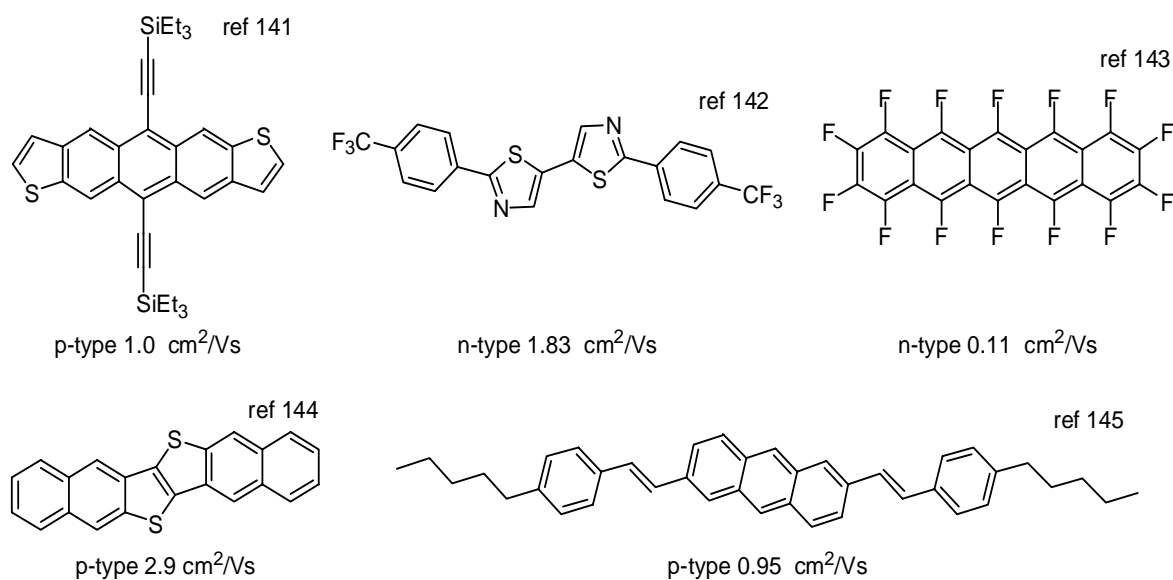
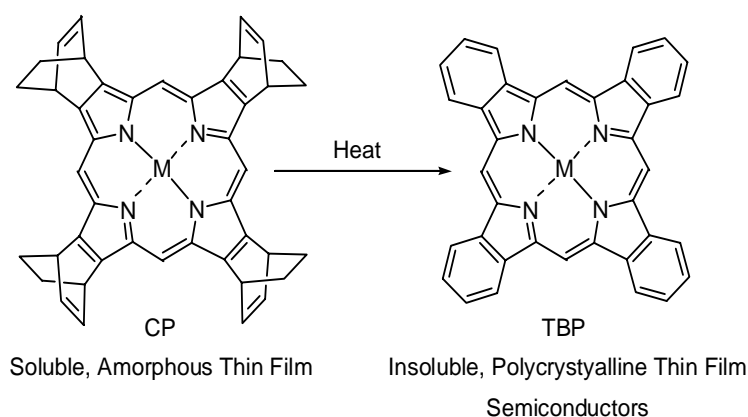


Figure 19 Recently Developed Semiconductors for OFET

A wide variety of organic semiconductors meet the requirement of performance of FET. However, they are mostly deposited on a device-substrate by thermal evaporation under high-vacuum conditions. To truly realize low cost, large area, and low temperature device fabrication, organic semiconductors must be deposited from solution with more economical and versatile techniques such as spin coating, drop casting and ink jet printing. Thus, development of solution-processable organic semiconductors is highly needed for realization of organic electronics. There are three classes of solution processable organic

semiconductors: polymer semiconductors,¹⁴⁶ soluble organic semiconductor precursors,¹⁴⁷ and organic semiconductors with long alkyl side chains.^{141,145} We are developing soluble precursors which are changed into insoluble semiconductors after coating by heating or irradiation of light. As the patterning and poly layers of semiconductors are possible by the method using precursors, the strategy using precursors has merits over other ones. However, it is not easy to get the pure sample due to the low solubility of them. In order to overcome this difficulty, we have introduced the retro Diels-Alder strategy in the field of porphyrin synthesis. Thus, TBP can be cleanly prepared by heating the precursor which has fused BCOD rings. Spin coating of the BCOD-fused porphyrin precursor followed by the retro Diels-Alder reaction gives an insoluble crystalline semiconductor film of TBP quantitatively. Spun cast films of the precursor exhibit amorphous, insulating behavior, following a thermal anneal in either vacuum or N₂, the amorphous film is converted into polycrystalline TBP, with crystal sizes exceeding 1 μm . Observed mobility of the devices exceed $10^{-2} \text{ cm}^2/\text{Vs}$ with appropriate process and device structure, and on/off current ratios exceeding 10^5 .¹⁴⁸



Scheme 8 Conversion of Soluble Precursors into Insoluble Semiconductors

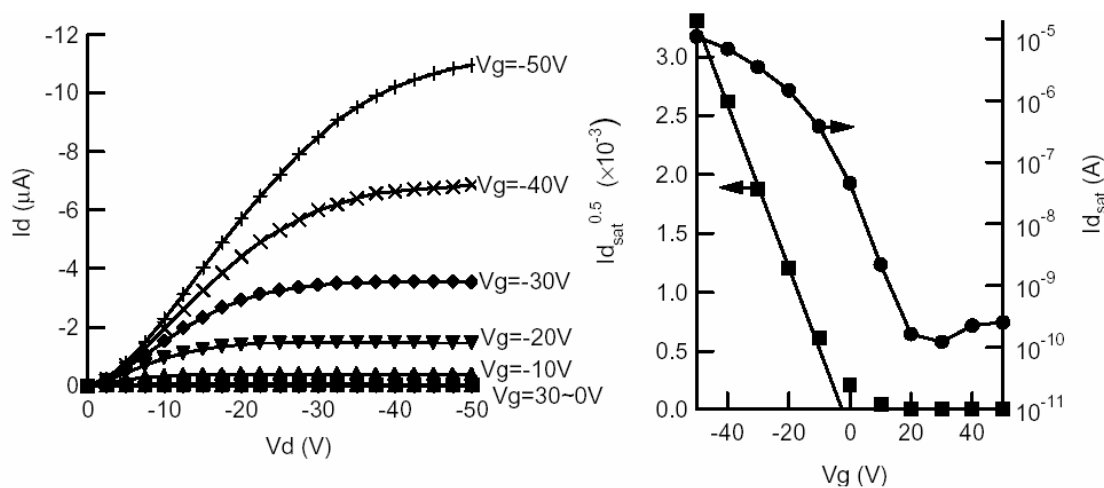


Figure 20 Transfer characteristics of a TBP OFET on SiO₂

OFETs using metal porphyrins such as CuTBP¹⁴⁹ or NiTBP¹⁵⁰ are also fabricated by a solution process, and they offer better performance of OFET as summarized in Table 1. It is remarkable that mobility of

CuBP and NiBP is higher than $0.1 \text{ cm}^2/\text{Vs}$, which is the highest value among OFETs based on porphyrins or phthalocyanines.

Table 2 OFET based on MTBP by Solution Process

material	mobility (cm^2/Vs)	V_{th}	on/off ratio
TBP	0.06	4	10^5
Cu-TBP	0.92(best 1.4)	5	2×10^5
Ni-TBP	0.4	9	3×10^4
Zn-TBP	0.013	12	500
Pd-TBP	1.1×10^{-3}	39	3

Soluble precursor of TBP is used not only for OFETs but also for thin film organic solar cells. Spin coating of soluble p- and n-type semiconductors provides a simple method for fabrication of solar cells as illustrated in Figure 21. TBP films on ITO electrodes (ITO/TBP) were prepared by continuous treatments of ITO electrodes with spin coating of soluble precursor, BCOD-fused porphyrin (CP), and thermal conversion from CP to TBP by heating up the electrodes. Photocurrent generation was observed by three-electrode system using ITO/TBP as a working electrode, Pt as a counter electrode, and Ag/Ag^+ as a reference electrode, using hexyl viologen (HV) as an electron acceptor. A two-layer structure of TBP and PCBM films and a three-layer structure of TBP, a mixture of TBP-PCBM, and PCBM films on ITO electrodes were also prepared by spin coating method. IPCE values up to 7 % were obtained for the three layer structure. Action spectra of three-layer structure showed overall visible light from 380 to 700 nm can be utilized to sensitize the photocurrent generation system.¹⁵¹

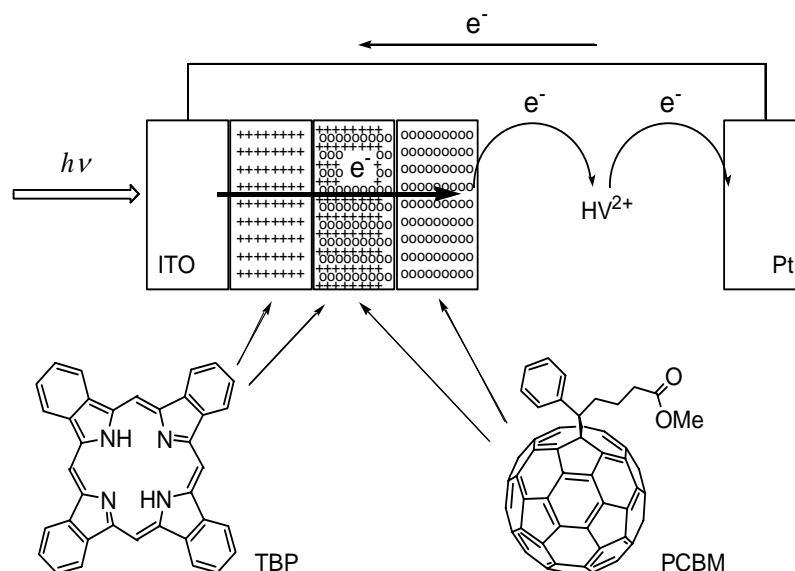


Figure 21 Organic Solar Cell by Spin Coating Soluble Semiconductors

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