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A New Synthesis of Porphyrins with Extended π-Conjugation and their Photophysics

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14. ABSTRACT
The contractor investigated the synthesis and characteristics of highly conjugated porphyrins, with the purpose to relate molecular structure to material properties. These molecules useful non-linear optical and optoelectronic properties. The contractor used a synthesis method based on the retro Diels-Alder reaction of porphyrins fused with bicyclo[2.2.2]octadiene units. This yields a new series of conjugated porphyrins that are difficult to be prepared by any other methods.

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tetrabenzoporphyrins

    (2)   a new synthesis of acenaphto- and fluotranthobenzoporphyrins

    (3)   synthesis of tetraanthroporporphyrins

    (4)   synthesis of meso alkinyl benzoporphyrins

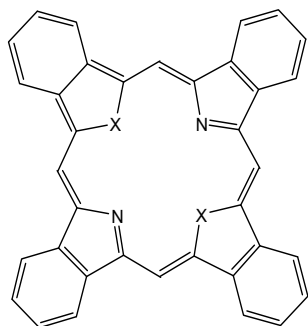   (5)   synthesis of tetrabenzoporphyrins and application to organic thin film transistors
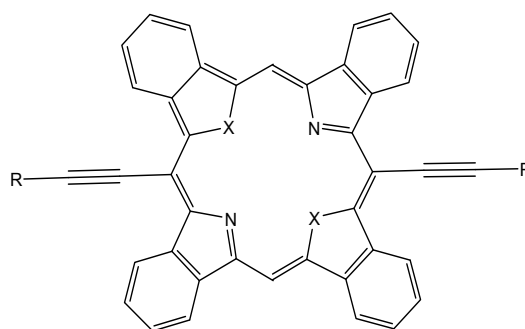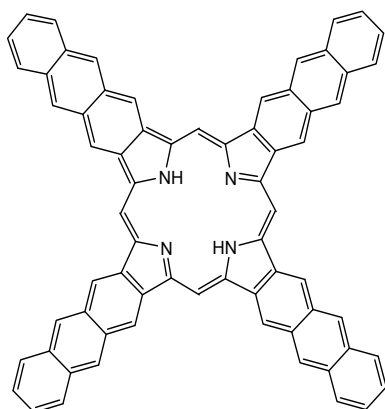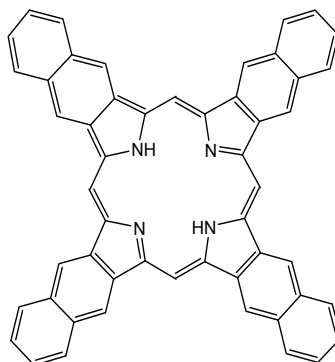
3. Collaboration with Dr. Paul Fleitz

4. Publications (2004-2006)

1. Accomplishments and Successes

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. We are developing a new method for the preparation of such p-conjugated porphyrins based on the retro Diels-Alder strategy. In general, p-conjugated molecules are difficult to be purified due to the low solubility. This difficulty is resolved by using the bicyclo[2.2.2]octadiene 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). We have already prepared tetrabenzoporphyrins and tetranaphthoporphyrins by this method. The research in 2004 was carried out to explore a new synthesis of other π-extended porphyrins or related compounds. We have succeeded in preparation of core modified tetrabenzoporphyrins, tetraanthroporphyrins, or meso alkynyl tetrabenzoporphyrins. Some of them are sent to Dr. Paul Fletiz at Air Force Laboratory in Dayton, Ohio to study their optical properties.
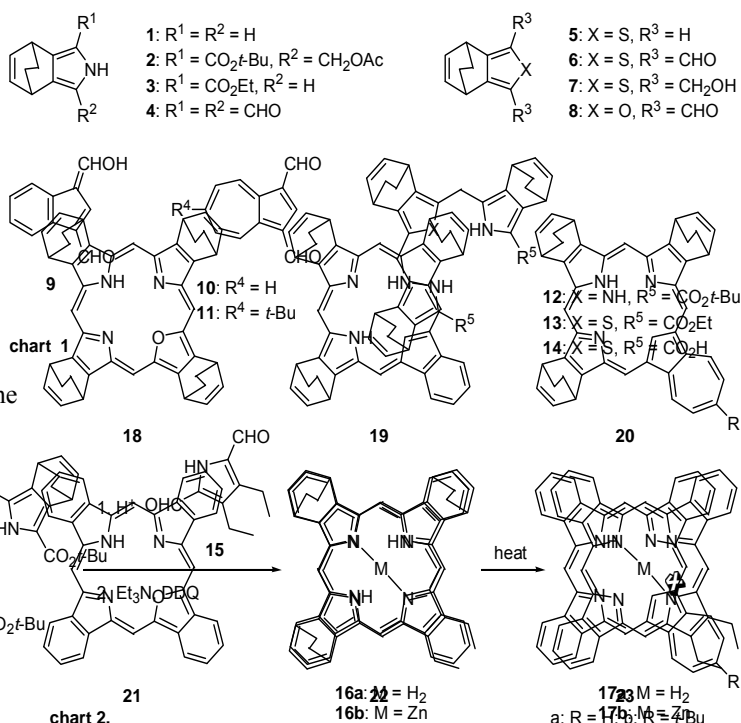
X = NH, S, O, C

2. Results and Discussion

Synthesis of Core Modified Tetrabenzoporphyrins (publication 2,3)

A bicyclo[2.2.2]octadiene-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.

In general, tripyrrane is synthesized by the reaction of 1,3-unsubstituted pyrrole with 2 molar amounts of 2-acetoxymethylpyrrole under acidic conditions. Montmorillonite K-10 clay catalyzed condensation of **1** with 2 molar amounts of **2** afforded tripyrrane **12** as pale brown crystals in high yield (>90%).

1: R^1 = R^2 = H
2: R^1 = CO$_2$t-Bu, R^2 = CH$_2$OAc
3: R^1 = CO$_2$Et, R^2 = H
4: R^1 = R^2 = CHO

5: X = S, R^3 = H
6: X = S, R^3 = CHO
7: X = S, R^3 = CH$_2$OH
8: X = O, R^3 = CHO

9

10: R^4 = H
11: R^4 = t-Bu

12: X = NH, R^5 = CO$_2$t-Bu
13: X = S, R^5 = CO$_2$Et
14: X = S, R^5 = CO$_2$H

chart 1

18

19

20

12

21

1. Et$_3$N, DDQ

15

16a: M = H$_2$
16b: M = Zn

heat

17a: M = H$_2$
a: R = H, b: R = t-Bu

Scheme 1.   chart 2.

Mass spectrum of **12** ionized by EI (70 eV) showed a molecular ion peak at *m/z* 659. Tripyrrane **12** was used in the reactions with dialdehydes without further purification. To demonstrate the utility of tripyrrane **12** for the preparation of porphyrinoid systems, [3+1] reaction of **12** with 4,5-diethylpyrrole-1,3-dicarbaldehyde (**15**) was conducted. Tripyrrane **12** was treated with trifluoroacetic acid to remove two *tert*-butyl ester groups. The resulting solution diluted with chloroform and treated with **15** overnight. The neutralization of the reaction mixture with triethylamine and the oxidation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) afforded **16a** in 23% yield. Porphyrin **16a** was converted into tribenzoporphyrin **17a** in quantitative yield by heating at 200 °C for 3 h *in vacuo*. Metal complex of **16a** was readily prepared by the treatment with zinc acetate. The product **16b** was also converted into **17b** (Scheme 1).

We then applied **12** to the synthesis of heteroporphyrins. The similar [3+1] reactions of **12** with **8**, **9**, **10**, and **11** under acidic con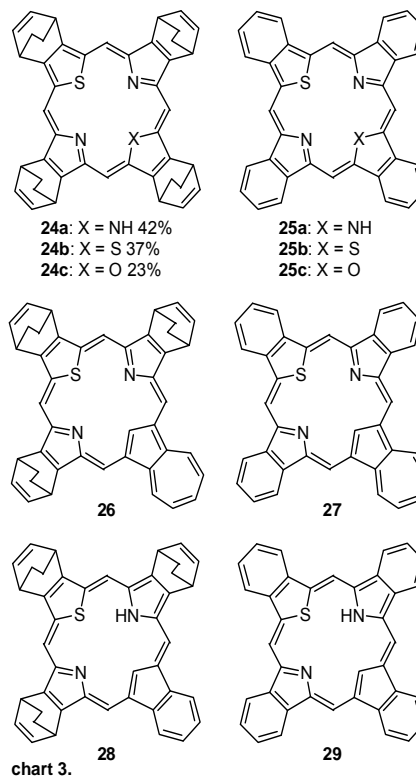dition, followed by the oxidation with DDQ or FeCl₃ afforded **18**, **19**, and **20** respectively, which were converted into the corresponding

π-expanded porphyrins **21**, **22**, and 16 in quantitative yields *via* retro Diels-Alder reaction. These compounds are stable and are easily characterized by physical and spectral methods including elemental analysis.

24a: X = NH 42%
24b: X = S 37%
24c: X = O 23%

25a: X = NH
25b: X = S
25c: X = O

Thiatripyrrane **13** was obtained by the reaction of **7**, which was obtained starting from **5** *via* formylation and reduction, with **1** in the presence of trifluoroacetic in 90% yield. The [3+1] reactions of thiatripyrrane **13** with **4**, **6**, **8**, **9**, and **10** under acidic condition, followed by the oxidation with DDQ afforded **24**, **26**, and **28**. they were heated at 230 °C in vacuo to give the corresponding π-expanded porphyrins **25**, **27**, and **29** in quantitative yields.

26

27

28

29

chart 3.

UV-Vis spectra of heteroporphyrins.

UV-Vis spectra of heteroporphyrins were measured in dichloromethane, DMF, or 1% TFA/dichloromethane. Both Soret and Q bands of tribenzoporphyrins (Soret bands: 413 nm (17a) and 416 nm (17b)) exhibited a bathochromic shift. compared with those of 16 (Soret bands: 392 nm (16a) and 400 nm (16b)). the similar bathochromic shift was observed in the cases of other π-expanded heteroporphyrins and BCOD-fused ones as shown in figures.
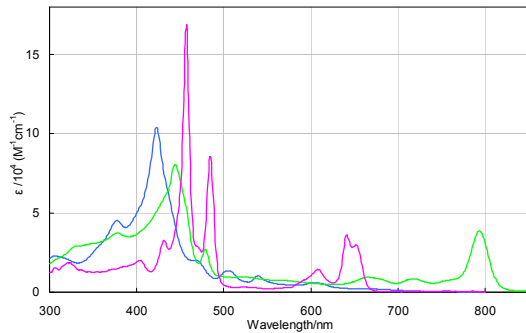
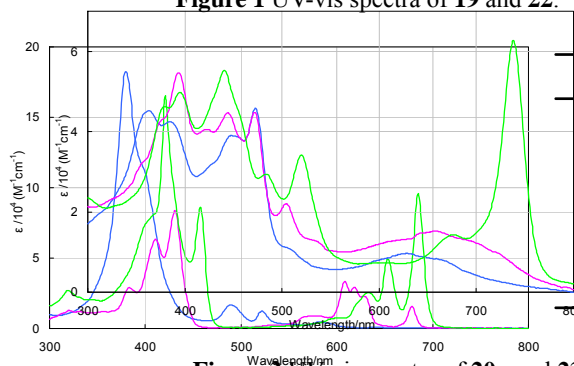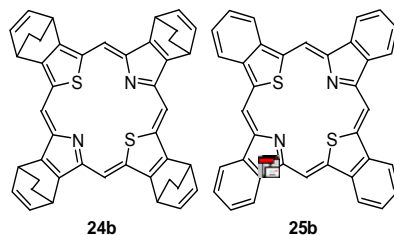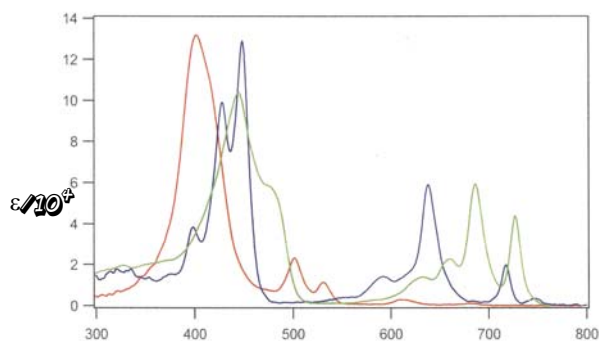|	solvent	λ_{max}, nm (log ε)
19	CH$_2$Cl$_2$	377 (4.66), 423 (5.02), 505 (4.13), 539 (4.01), 603 (3.78), 660 (3,35)
22	DMF	404 (4.03), 431 (4.52), 457 (5.23), 484 (4.93), 608 (4.16), 641 (4.56), 652 (4.48)
22	1%TFA /CH$_2$Cl$_2$	378 (4.57), 444 (4.91), 479 (4.43), 666 (3.97), 718 (3.93), 794 (4.59)

Figure 1 UV-vis spectra of **19** and **22**.

	solvent	λ_{max}, nm (log ε)
20a	CH$_2$Cl$_2$	363 (4.86), 385 (4.63), 448 (4.59), 473 (4.66), 629 (3.99)
23a	DMF	394 (4.74), 444 (4.65), 472 (4.65), 505 (4.34), 657 (4.18)
23a	1%TFA /CH$_2$Cl$_2$	608 (4.12), 671 (4.47), 702 (4.56), 678 (3.19), 738 (3.805)

	solvent	λ_{max}, nm (log ε)
18	CH$_2$Cl$_2$	380 (5.26), 489 (4.22), 522 (4.09), 582 (3.68)
21	DMF	383 (4.46), 411 (4.80), 431 (4.92), 520 (4.53), 676 (4.15)
21	1%TFA /CH$_2$Cl$_2$	421 (5.22), 458 (4.93), 633 (4.41), 653 (4.69), 685 (4.98)

Figure 3 UV-vis spectra of **20a** and **23a**.

Figure 2 UV-vis spectra of **18** and **21**.

24b   **25b**

24b in CH$_2$Cl$_2$ (red line)

25b in DMF (blue line)

25b in 1% TFA/CH$_2$Cl$_2$ (green line)
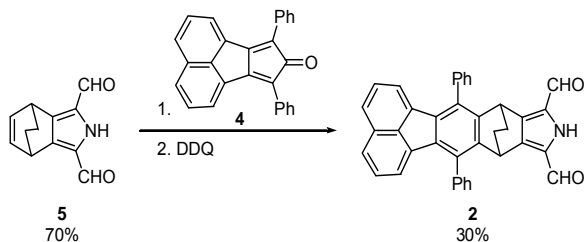
Figure 4 UV-vis spectra of 24b and 25b.

(2) A new synthesis of acenaphto- and fluoranthobenzoporphyrins (publication 14)

Benzoporphyrins fused with acenaphthylene or fluoranthene and were prepared by the condensation of bicyclo[2.2.2]octadiene(BCOD)-fused tripyrrane with appropriate pyrrole dialdehydes and the subsequent retro Diels-Alder reaction. The absorptions of these new porphyrins were very intense at both Soret and Q bands.
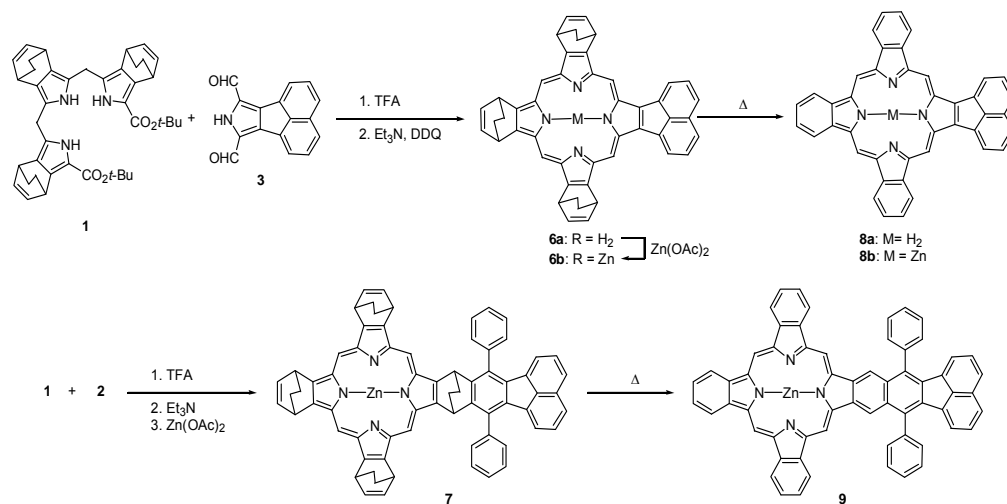
Synthesis

BCOD-fused tripyrrane 1 was obtained with mild conditions using montmorillonite K-10 in dry CH$_2$CL$_2$ at room temperature. Tripyrrane 1 was used without purification for 3+1 porphyrin synthesis, as it was decomposed during purification by column chromatography with silica gel. Fluoranthoisoindole-1,3-dicarbaldehyde 2 and acenaphtho[1,2-c]pyrrole-2,9-dicarbaldehyde (3) were used as pyrrole dialdehydes. Dialdehyde 2 was prepared by the Diels-Alder reaction of 7,9-diphenyl-8H-cyclopenta[l]acenaphthylen-8-one 4 with isoindole-1,3-dicarbaldehyde 5 followed by oxidation with DDQ. A mixture of crude tripyrrane 1 and 3 in CHCL$_3$ containing TFA was stirred at room temperature for 11 h followed by oxidation with DDQ to give porphyrin 6a in 14 % yield. Porphyrin 6a was converted into the zinc complex 6b on treatment with Zn(OAc)$_2$. The similar reaction of 1 with 2 yielded the corresponding porphyrins. Heating 6a at 230 C for 3 h in vacuo resulted in clean retro Diels-Alder reaction to give acenaphthotribenzoporphyrin 8a in quantitative yield. Zinc complex
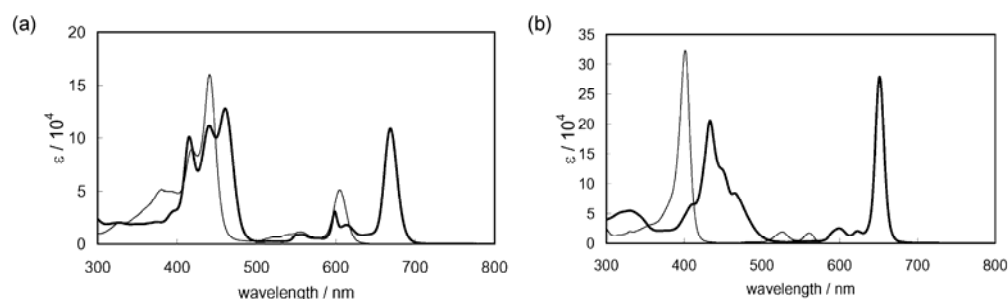
was also converted into 8b, which proceeded slightly at lower temperature (200 C) for 3 h. The retro Diels-Alder reaction of 8b proceeded stepwise at 170 and 270 C by TG analyses. At first, three ethylene units were eliminated from BCOD rings and then another ethylene unit was eliminated by heating. When 7 was heated at 270 C for 3 h, the color of the crystals was changed from red to deep green to give zinc complex 9 in quantitative yield without purification.

The absorption data of porphyrins are summarized in Table 1. Some typical spectra are shown in Figure 1. The absorption spectra of BCOD-fused porphyrins were similar to those of typical β-substituted porphyrins like octaethylporphyrin. Spectra of them were dramatically changed by the retro Diels-Alder reaction as shown in Figure 1. The Q bands of 8 and 9 were highly red shifted and very intense compared to those of symmetrical benzoporphyrin. The Soret bands of them were also very intense with large molar absorptivity over 10^5 $M^{-1}cm^{-1}$.

Table 1. Absorption Maxima of Porphyrins

sample	solvent	λ_{max}, nm (log ε)	
6a	CH$_2$Cl$_2$	385 (4.83), 430 (5.07)	523 (4.07), 564 (4.45), 584 (4.17), 650 (3.93)
6b	CH$_2$Cl$_2$	419 (4.95), 441 (5.20)	555 (4.06), 605 (4.71)
7	CH$_2$Cl$_2$	401 (5.51)	526 (4.28), 561 (4.23)
8a	DMF	421 (4.69), 438 (4.85), 461 (4.74)	540 (4.00), 572 (4.33), 633 (3.62), 691(4.58)
8b	DMF	415 (5.00), 440 (5.05), 461 (5.11)	556 (3.96), 599 (4.48), 613 (4.26), 669 (5.04)
9	DMF	433 (5.31), 465 (4.93)	599 (4.40), 623 (4.31), 651 (5.45)

FIGURE 1. UV-Vis spectra of (a) 6b (solid line) in CH$_2$Cl$_2$, 8b (bold line) in DMF. (b) 7 (solid line) in CH$_2$Cl$_2$, and 9 (bold line) in DMF.

(3) Synthesis of Tetraanthoroporphyrins (unpublished)

Linearly π-expanded porphyrins, such as tetrabenzoporphyrins (TBPs) and tetranaphthoporphyrins (TNPs), have attracted great attention for the applications such as dyestuffs, optical materials, nonlinear optics, conducting materials, photosensitizers for photodynamic therapy (PDT), solar systems, and so on.[1] Although TBPs and TNPs have already been prepared by several synthetic methods,[1,2,3] the highly π-expanded family, tetraanthroporphyrins (TAnPs), has been prepared only as a complex mixture probably because of the low solubility of the planar porphyrin in various solvents and the low stability.[4,5]
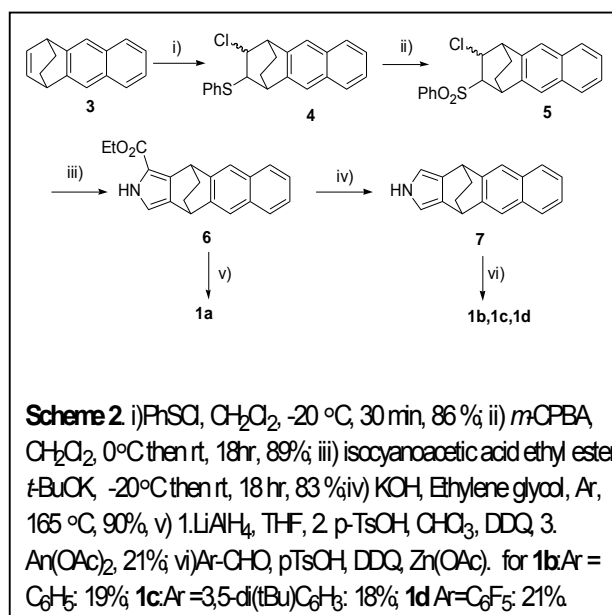
Recently we have developed an efficient synthetic method of various benzoporphyrin-type

1a : R = H
1b : R = Ph
1c : R = 3,5-di-*t*Bu
1d : R = C₆F₅

2a : R = H
2b : R = Ph
2c : R = 3,5-di-*t*Bu
2d : R = C₆F₅

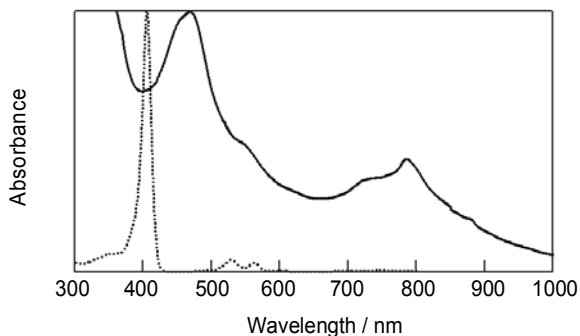compounds including TBPs and TNPs using retro-Diels-Alder reaction.[6,7] With this method, the soluble porphyrins fused with bicyclo[2.2.2]octadine were converted quantitatively into insoluble benzoporphyrins only by heating at around 200 or 290 °C, which were decided by Tg and DSC meas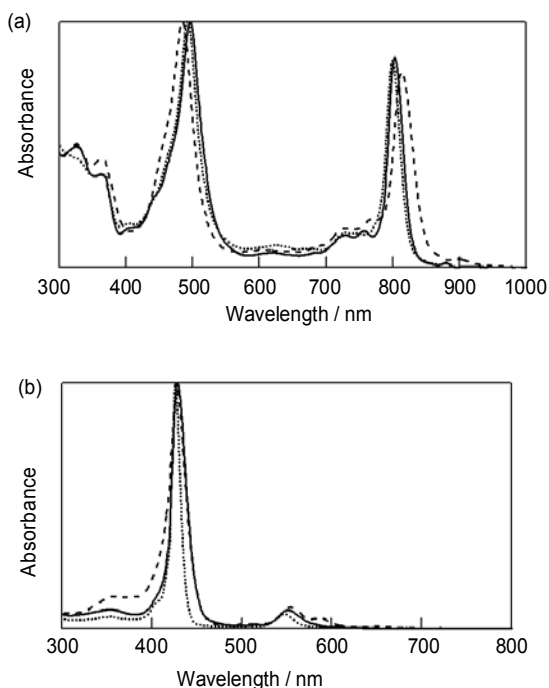urement. As the thermal process does not require any reagents, solvents, or purification steps, it is the ideal method for the preparation of the low-soluble and highly planar π-conjugated porphyrins. Recently Aramaki et. al.[8] revealed that TBP film prepared by spin coating of bicyclo[2.2.2]octadine-fused porphyrin on silicon substance followed by the heating showed good performance as organic semiconductors for transistor applications comparable with pentacene. So more π-expanded systems, such as TAnPs, might be promising candidate for organic device. Here we report the novel synthesis of TAnPs **2a-d** from the bicycloporphyrin precursors 1a-d for the first time (Scheme 1).

Scheme 2. i)PhSCl, CH₂Cl₂, -20 °C, 30 min, 86 %; ii) *m*-CPBA, CH₂Cl₂, 0°C then rt, 18hr, 89%; iii) isocyanoacetic acid ethyl ester *t*-BuOK, -20°C then rt, 18 hr, 83 %;iv) KOH, Ethylene glycol, Ar, 165 °C, 90%, v) 1.LiAlH₄, THF, 2. p-TsOH, CHCl₃, DDQ, 3. An(OAc)₂, 21%; vi)Ar-CHO, pTsOH, DDQ, Zn(OAc). for **1b**:Ar = C₆H₅: 19%; **1c**:Ar =3,5-di(tBu)C₆H₃: 18%; **1d**: Ar=C₆F₅: 21%.

Figure 1

Figure 2 UV-vis absorption spectra of (a) TAnPs and (b) their precursors. 1B

The preparation of the TAnPs are shown in Scheme 1and 2. An addition of phenylsulfenyl chloride to 1,4-dihidro-1,4-etanonanthracene6 at -20 °C gave the compound 3 in 86 % yield and the oxidation of 3 with m-CPBA gave 4 in 89 % yield.7 When the dry THF solution of 4 was treated with isocyanoacetate ethyl ester in the presence of 2.7 eq. of t-BuOK at -20 °C, followed by the stirring at rt for 18hr gave the pyrrole 5 in 89 % yield. The treatment of the pyrrole 5 with potassium hydroxide gave isoindole **6**. The porphyrin **1a** was prepared from the pyrrole **5** in 2steps; 1) the reduction of pyrrole **5** by LAH; 2) the acid catalyzed condensation in $CHCl_3$ in the presence of *p*-toluenesulfonic acid, followed by the oxidation with DDQ and the metalation with $Zn(OAc)_2$. The porphyrin **1b** and **1c** were prepared by the acid condensation of isoindole **6** with aldehydes in the presence of TFA followed by oxidation with DDQ and metalation. Porphyrins **1** were converted into pure TAnPs **2** quantitatively by heating at around 300 °C in vacue for 10 min (Scheme 1). The temperature of the retro Diels-Alder reaction was decided by Tg measurement. The porphyrins **1** were characterized by ^{1}H NMR spectroscopy, FAB or MALDI-TOF MS spectroscopy, and elemental analysis. Since the solubility of the tetraanthroporphyrin **2a** was quite low after the retro Diels-Alder reaction because of the planarity, characterization of porphyrin **2a** was confirmed only by mass spectroscopy and UV-vis absorption spectra (Figure 1). Since the absorption spectrum of
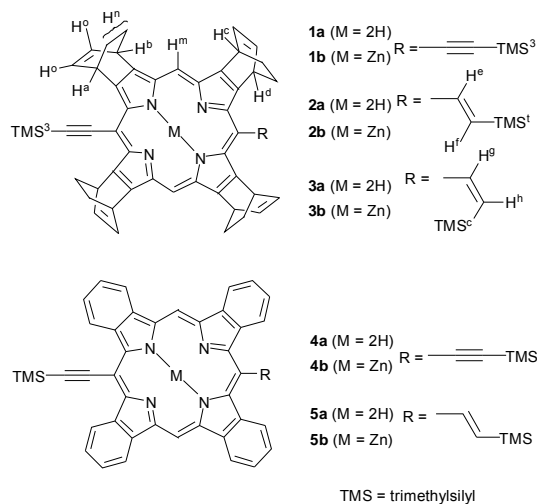
the anthroporphyrin **1a** is quite broad, porphyrins are thought to be stacked by π-π interaction in the solution.

In order to improve the solubility, *meso* positions of the anthroporphyrin were substituted with the aromatic rings such as phenyl, 3,5-di(tBu)-ph, and 4-fluorophenyl groups. The solubility of the porphyrins was improved, and the ^{1}H NMR measurement of the porphyrin **2b**, **2c**, and **2d** were possible in CDCl$_3$.
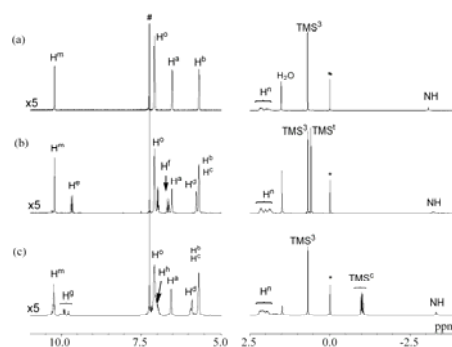
The absorption spectra of **2b**, **2c**, and **2d** and their precursor porphyrins **1b**, **1c**, and **1d** are shown in Figure 2. Because of the π-expansion, the broadening and red shifts of Soret and Q bands are observed.   Furthermore the absorption of the Q band is strong as much as Soret band.   The trend of the change and the shift of the absorption spectra are consistent with the results of the molecular orbital calculations.[8] When the TAnPs were kept in solution under air atmosphere, the shape of the absorption spectra changed in several hours. To know the reason of the spectra change, mass spectra of **2a** were measured.   Then additionally to the parent peak, M^++32 mass was observed, probably because of the [2+4] addition reaction of oxygen to the molecule.   This reactivity of the porphyrin to oxygen would have been one of the reasons that TAnPs have been little reported.

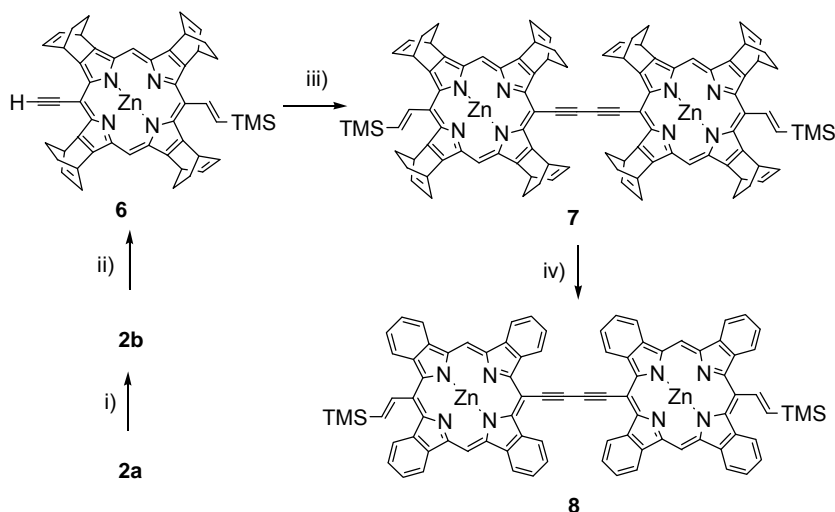# (4) SYNTHESIS OF MESO-ALKYNYL TETRABENZOPORPHYRINS (PUBLICATION 12)

Highly conjugated porphyrins and metalloporphyrins have attracted strong attention in connection with unusual electro-optical and non-linear optical properties such as two-photon absorption. Alkynyl substituents are the most effective way of making conjugated connections to the *meso* positions of porphyrins and 5,15-dialkynylporphyrins are useful building blocks for making highly conjugated porphyrin oligomers.   Additionally, tetrabenzoporphyrins (TBPs) and related

1a (M = 2H)
1b (M = Zn) R =   TMS[3]

2a (M = 2H) R =
2b (M = Zn)

3a (M = 2H) R =
3b (M = Zn)

4a (M = 2H)
4b (M = Zn) R =   TMS

5a (M = 2H) R =
5b (M = Zn)

TMS = trimethylsilyl

π-expanded complexes show intriguing optical properties in the near-infrared region and are very attractive for applications such as non-linear optical materials, optical memories, and opto-electronic materials. Considering these properties, π-expanded oligomers of TBPs connected by alkynyl substituents at the *meso* positions might be promising highly conjugated materials. However, to our knowledge, such materials have rarely been reported because of the low solubility of TBPs in common organic solvents. Recently we and others have reported soluble precursors of TBPs which, after purification,

Fig. 1. ^{1}H NMR spectra of porphyrin (a) **1a**, (b) **2a**, and (c) **3a** in CDCl$_3$.

could easily be converted to TBPs. Using our method, we have tried to prepare 5,15-dialkynyl TBP **4a** from bicyclo[2.2.2]octadiene (BCOD) ring-fused 5,15-dialkynylporphyrin **1a** via the retro Diels-Alder reaction. During the synthesis of **1a** by [2+2] acid-catalyzed condensation of a dipyrrylmethane, and unsymmetrical 5-alkenyl-15-alkynyl-porphyrin **2a** was obtained unexpectedly in addition to the targeted porphyrin **1a**. The ^{1}H NMR spectrum of **2a** is shown in Fig. 2 with that of porphyrin **1a** for comparison. As far as we know, a few 5-alkenyl-15-alkynylporphyrins, which have been prepared by a partial nucleophilic addition to dialkynylporphyrin or a long multistep synthesis, have been reported so far. With the [2+2] acid-catalyzed synthesis using substituted propynal, only 5,15-dialkynyl porphyrin has been reported.
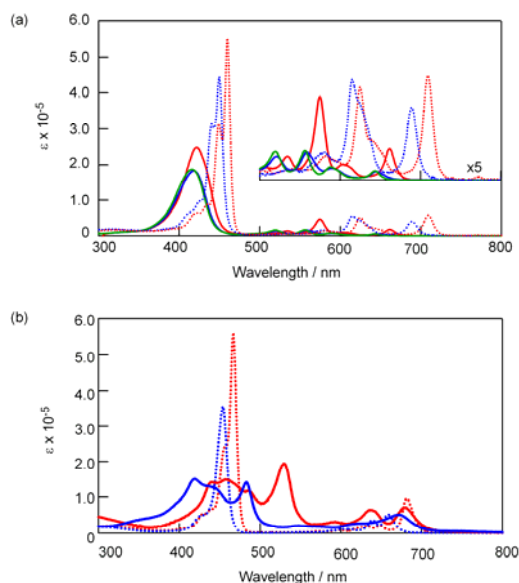

Scheme 2. Synthesis of the dimers **11** and **12**. Reagents and conditions. i) Zn(OAc)$_2$·2H$_2$O, CHCl$_3$, 75 °C, 2h, 85%; ii) K$_2$CO$_3$, THF, 70 °C, 5 h, 99%; iii) CuCl, TMEDA, O$_2$, CH$_2$Cl$_2$, rt, 20 min, 33%; iv) 200 °C, 10 min, quant..

This 5-alkenyl-15- alkynylporphyrin **2a** is a very attractive building block, butadiyne-linked porphyrin oligomers and dimers, since selective cleavage of the trimethylsilyl (TMS) group on either especially for the synthesis of the vinyl or alkynyl end is possible by exploiting the different reactivities of the two TMS groups. Selective cleavage of the TMS group of the unsymmetrical porphyrin **2b** gave the porphyrin **6** and Glaser-Hay coupling of **6** gave porphyrin dimer **7** in 33% yield (Scheme 2). It was possible to convert dimer **7** quantitatively to benzoporphyrin dimer **8** by heating it to 200 °C under vacuum. Since Zn complexes of TBP monomers and dimers were poorly soluble in common organic solvents, such as CH_2Cl_2 and THF, their absorption spectra were measured in DMF (7×10^{-7} M) as shown in Fig. 2. The absorption spectrum of dimer **7** showed broadening and splitting of the Soret band, as has been reported for butadiyne-linked porphyrin dimers in CH_2Cl_2. This splitting has been explained by the simple point-dipole exciton coupling theory developed by Kasha. The TBP dimer **8** showed a more blue-shifted Soret band at 530 nm and relatively strong Q bands at 636 and 680 nm.
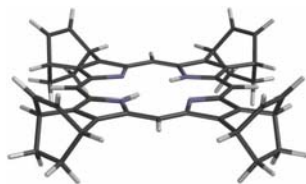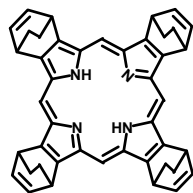

Fig. 2 UV-vis absorption spectra of (a) porphyrins **1a** (red solid line), **2a** (blue solid line), **3a** (green solid line), **4a** (red dotted line), and **5a** (blue dotted line) in CH_2Cl_2; and (b) zinc porphyrin monomers **4b** (red dotted line) and **5b** (blue dotted line), and dimers **7** (red solid line) and **8** (blue solid line) in DMF.

In conclusion, we have found a novel one-pot synthesis of 5-alkenyl-15-alkynyl porphyrin **2**, and have succeeded in preparing the TBP dimer in moderate yield by selective desilylation of porphyrin **2b**. The further development of these unsymmetrical porphyrins to the higher oligomers by selective cleavage of the TMS or TIPS group is under investigation.

(5) Synthesis of tetrabenzoporphyrins and their application to organic thin film transistors (Publication 1, 8, 9, 10, 11, 15)

Tetrabenzoporphyrins and phthalocyanines are important in the filed of material sciense, they can be used as semiconducting materials, near IR dyes, or nonlinear optical materials. 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, tetrabenzoporphyrin can be cleanly prepared by heating the precursor which has fused bicyclo[2.2.2]octadiene(BCOD) rings. This strategy can be extended to synthesis of a series of highly conjugated porphyrin analogues, including thia-, dithia- and oxathia-tetrabenzoporphyrins. Furthermore, carba-tetrabenzoporphyrins and phthalocyanines are also prepared by this method. Organic field effect transistors (OFET) have merits that inorganic devices can hardly have, such as low cost, large asrea, and low temperature device fabrication. They have been under extemsive development for display and IC tag applications, making use of the advantages.Spin coating of the BCOD-fused porphyrin precursor followed by the retro Diels-Alder reaction gives an insoluble crystalline semiconductor film of tetrabenzoporphyrin quantitatively. Field effect transistors can be fabricated by this method. Observed mobilities of the devices exceed 10^{-2} cm^2/Vs with appropriate process and device structure. Its FET performance is related to its purity, device structure, and fabricatoon process. The solid state structure of the film is dependent on the fabrication process and the substrate, which is related the device perfomance. Thus, the retro Diels-Alder strategy provides an important method for preparation of benzoporphyrins and their derivatives.
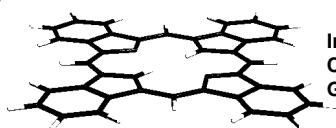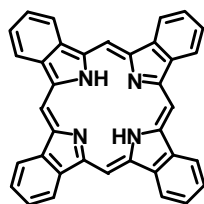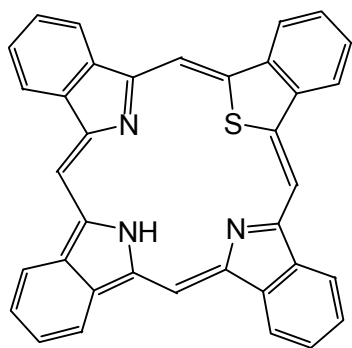
Soluble
Amorphous Film
 (Good Morphology)
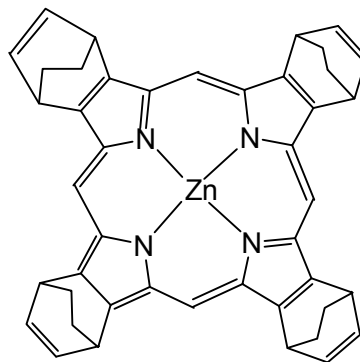
Heating
(Conversion)

Elimination of
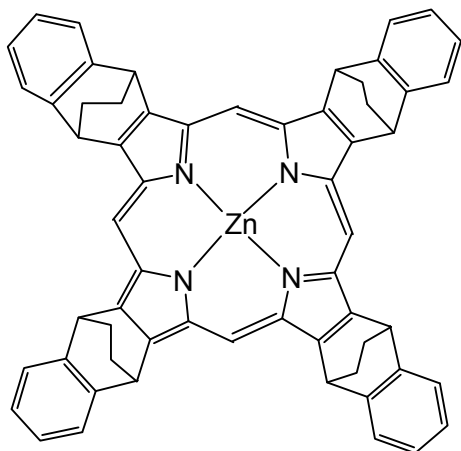4 Ethylene Molecules

Insoluble
Crystalline
Good Semiconductor

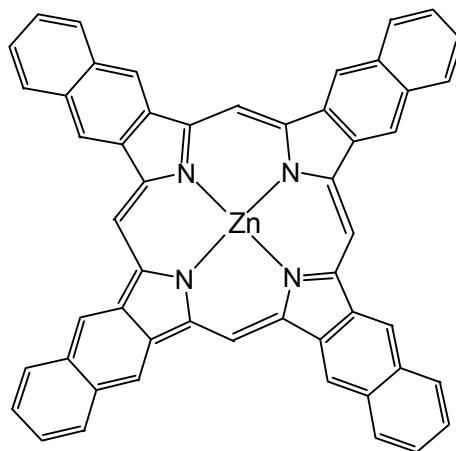# 2. COLLABORATION WITH DR. PAUL FLEITZ
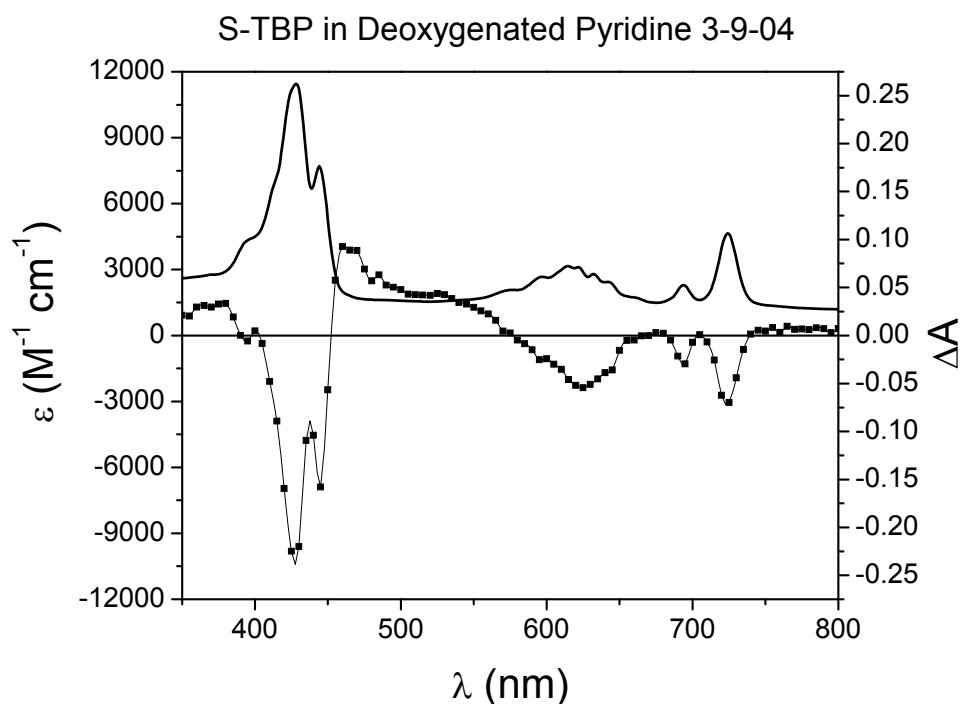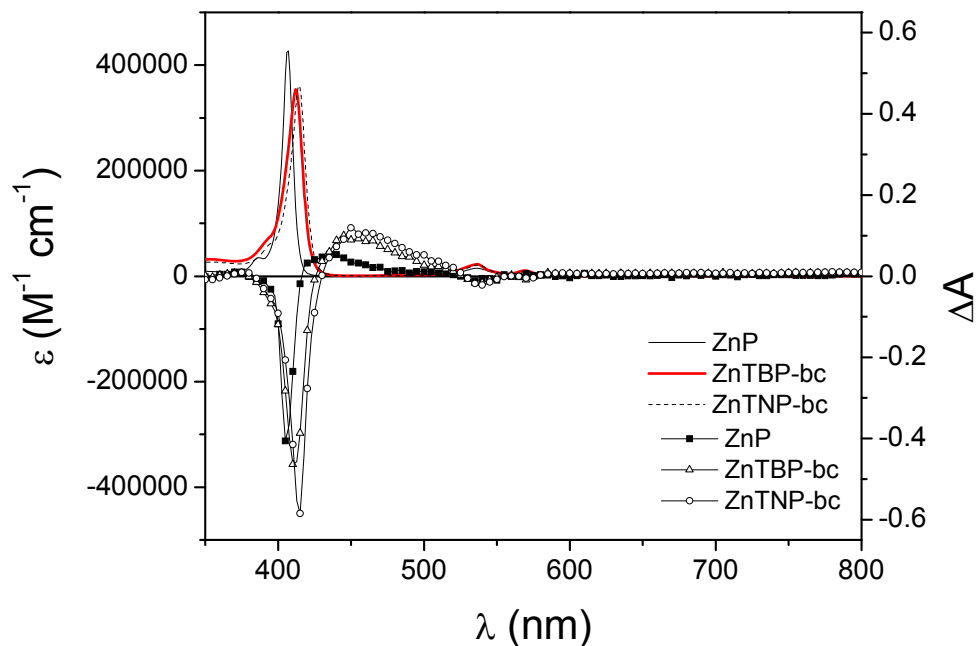
S-TBP

ZnTBP-bc

ZnTNP-bc

ZnTNP

Shown above are the structures of the four chromophores recently sent by Professor Noboru Ono from Japan. The ground state extinction coefficient of each was measured as well as the triplet

excited state difference spectrum. neither s-tbp or zntnp were

very soluble and therefore it was not possible to obtain accurate

values for the molar extinction coefficients of these materials.

the values on the graphs for these two molecules are probably

much lower than the actual molar extinction coefficient for these

molecules.

S-TBP in Deoxygenated Pyridine 3-9-04

For s-tbp the ground state spectrum is different than that

typically observed for porphyrin materials. the spectrum contains

an absorbance feature around 600 nm which is likely the result of

the core modifications that have been made in this material. The excited state transient absorbance spectrum has a peak maximum at 460 nm. The transient was found to decay biexponentially with a lifetime of $\tau_1 = 18$ μs and $\tau_2 = 117$ μs. The ground state absorbance actually became larger following laser irradiation. Laser irradiation may have heated of the solution which increased the solubility of the material.
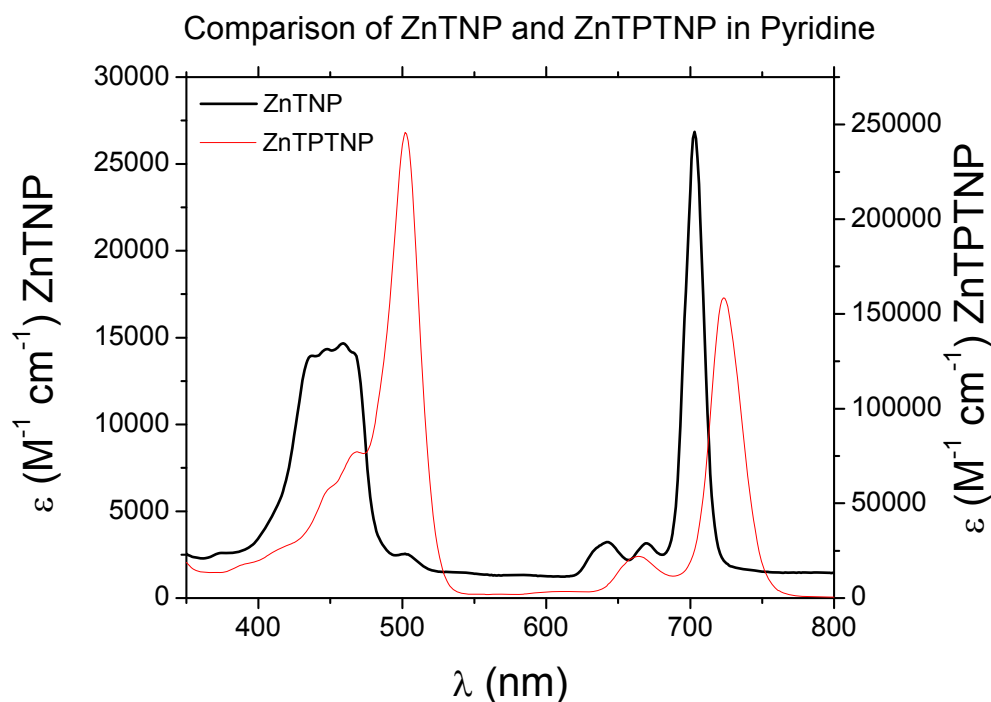

The spectra for ZnTBP-bc and ZnTNP-bc compared to ZnPorphyrin (ZnP)

are shown above. There is very little difference in either the ground state or excited state spectra of these materials. This is not surprising since these precursor materials do not have conjugation extending beyond the central porphyrin core. Both the ZnTBP-BC and ZnTNP-BC decayed with biexponential kinetics. The first lifetime is 170 μs and 207 μs for ZnTBP-BC and ZnTNP-BC, respectively. The long-lived transient gave an unreliable value for decay which was longer than 1 ms.

Shown below are the ground state absorbance spectra of ZnTNP (from Professor Ono) and ZnTPtNP (from our own laboratory). The molar absorption coefficients we observed for ZnTNP are an order of magnitude smaller than that measured for ZnTPtNP. As mentioned earlier, this is almost surely due to the poor solubility of this material and the limited accuracy of our technique. Interestingly the B-band of the ZnTNP is not resolved in our spectrum. Data on this molecule in the literature from a Russian group in 1985 has a much

better resolved spectrum in this region. It is not completely clear to us why this feature was not better resolved. Initially we believed it to be the result of the saturation of the signal. But this does not appear to be the case since the more intense Q-band is fully resolved. We did observe an upward curvature in the plot of absorbance versus concentration in ZnTNP, which indicates a possible aggregation.

Comparison of ZnTNP and ZnTPTNP in Pyridine

we also measured the excited state absorption of ZnTNP and

compared this Data to previous Data on ZnTPTNP. This is shown below. The excited state absorption is broader in the case of ZnTNP, which follows what we previously thought. This chromophore decays with single exponential kinetics with a lifetime of 110 μs in Deoxygenated pyridine. Also with this material we found that the ground state absorbance becomes larger with irradiation indicating that heating by the laser may assist solubility of this material.

Comparison of ZnTNP and ZnTPTNP in Deoxygenated Pyridine

Based on these brief studies it is apparent that ZnTNP is a compound of interest. However, solubility is an issue (which we knew would be). It would be of interest to come up with ways to increase solubility without changing the chromophores photophysical properties.

2. Publications (2004-2006)

(1) Solution Processible Organic Semiconductor for Transistor Applications: Tetrabenzoporphyrin. S. Aramaki, Y. Sakai, N. Ono, *Appl. Phys. Lett.* 84, 2085 (2004).

(2) First Synthesis of a Series of Core Modified Tetrabenzoporphyrins. Y. Shimizu, Z. Shen, T. Okujima, H. Uno, N. Ono, *Chem. Commun.* 374 (2004).

(3) An efficient synthesis of conjugation-expanded carba- and azuliporphyrins using a bicyclo[2.2.2]octadienes fused tripyrrane. T. Okujima, N. Komobuchi, Y. Shimizu, H. Uno, N. Ono, *Tetrahedron Lett.* 45, 5461 (2004).

(4) Controlling conformations and physical properties of

meso-tetrakis(phenylethynyl)porphyrins by ring fusion. Z. Shen. H. Uno. Y. Shimizu. N. Ono. organic bio. chem.. 3442 (2004).

(5) a doubly n-fused benzohexaphyrins and its rearrangement to a fluorescent macrocycle upon DDQ oxidation. Y. Inokuma. T. Matsunari. N. Ono. H. Uno. A. Osuka. angew. chem. int. ed.. 44. 1856 (2005).

(6) photochemical synthesis of pentacene and its derivatives. H. Yamada. Y. Yamashita. M. Kikuchi. H. Watanabe. T. Okujima. H. Uno. T. Ogawa. K. Ohara. N. Ono. chem. eur. J. 11. 6212 (2005).

(7) electron transfer reaction of cu(ii)porphyrin cimplex: effect of structural deformation on the electron self exchange rate. M. Imaho. K. Aoki. N. Ono. H. D. Takagi. inorganic chem. commun.. 8. 979 (2005).

(8) structural. optical. and photophysical properties of ni(ii)alkylthioporphyrins. insight from experimental and DFt/DDFt studies. inorganic. chem.. 44. 6609 (2005).

(9) methanofullerene-coated tetrabenzoporphyrin organic field effect transistors. P. B. Shea. J. Kanichi. Y. Cao. N. Ono. appl. phys. lett.. 87. 173506 (2005).

(10) electrical prperties of staggered electrode. solution-processed. polycrystalline tetrabenzoporphyrin field-effect transistor. P. B. Shea. A. R. Johnson. N. Ono. J. Kanichi. ibbe. trans. elec. devices. 52. 1497 (2005).

(11) fiels-effect mobility of polycrystalline tetrabenzoporphyrin thin-film transistors. P. B. Shea. J. Kanichi. N. Ono. J appl. phys.. 98. 014503 (2005).

(12) novel one pot synthesis of 5-alkenyl-15-alkynylporphyrins and their derivatisation to a butadiyne-linked benzoporphyrin dimmer. H. Yamada. K. Kusibe. T. Okujima. H. Uno. N. Ono. chem. commun.. 383 (2006)..

(13) fluorecent probe for na⁺. synthesis and

Spectroscopic Studies of Exocyclic Ring-Fused Boron Dipyrromethene Dyes. X. H. Yun, S. Zen, T. Okujima, N. Ono. Chinese J. of Inorganic Chem. 22, 801 (2006)..

(14)   A New Synthesis of Acenaphotobenzoporphyrin and Fluoranthobenzoporphyin. T. Okujima, N. Komobuchi, H. Uno, N. Ono. Heterocycles. 67, 255 (2006).

(15)   Solution-Processed Nickel Tetrabenzoporphyrin Thin-Film Transistors. P. B. Shea, J. Kanicki, L. R. Pattison, P. Petroff, H. Yamada, N. Ono, J. Appl. Phys. 100, 034502 (2006).