

Porphyrin Supramolecules as Materials for Photosynthesis and Third Order Nonlinear Optics

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Imidazolyl-substituted porphyrinatoZn gave a complementary dimer of slipped cofacial orientation showing an extremely large stability constant amounting 10^{10} M^{-1} in a CHCl_3 solution. It mimicked precisely the structure of special pair of bacterial photosynthetic reaction center. Bridging of two imidazolylporphyrinatoZn units directly at meso-meso positions afforded a way to extend the complementary coordination structures to porphyrin arrays of few hundreds nanometer scale. When two imidazolylporphyrinatoZn complexes were linked by a *m*-phenylene bridge, the oligomers initially obtained were converged into a mixture of hexameric and pentameric macrocycles under dilute condition. The ring mimicked the structure and function of light harvesting complexes of bacterial photosynthetic systems. *Meso-meso* linked and butadiyne-bridged bis(imidazolylporphyrinatoZn) complex were terminated optionally with free base porphyrins. There exhibited excellent properties of 3rd order nonlinearities and two photon absorptions.

Key words: Photosynthesis, complementary coordination, antenna ring, nonlinear optics

1. INTRODUCTION

X-ray crystallography of light-harvesting complex from photosynthetic purple bacteria has been determined in 1995. It elucidated a beautiful ring structure of B850, where 18 bacteriochlorophylls, or more precisely nine dimeric units, are arranged in a barrel structure.[1] The ring is constructed from coordination of histidyl imidazolyl substituent to the Mg center without any covalent bondings to the supporting transmembrane helices, which are arranged in inner and outer rings of nine components each. To our surprise, the arrangement of the dimer unit resembled to the structure of special pair of the most important pigment in the photosynthetic reaction center, which had already been analyzed in 1984 as the first successful X-ray crystal structure of membrane proteins.[2] Two chlorophylls face to each other with almost parallel orientation of large π -orbitals with a little bit of slipping distance to each other, i.e., slipped cofacial arrangement, which had been reported already from our laboratory in 1994. Immediately after this discovery, we decided to construct such the antenna structure and the function as well, as a challenging target by the use of supramolecular methodology.

At the same time, the light harvesting complex is regarded as an effective medium to transfer excitation energy without any energy dissipation. It may also be regarded as attractive material for molecular electronic or photonic applications. Much attention has been paid recently on these

materials after the miniaturization of metal-oxide-semiconductor-based large-scale integration by physical approach comes close to its absolute limit. Porphyrin has a large conjugated π -electron system which absorbs UV and visible light by their small HOMO-LUMO energy gap. Its light absorbing and emitting properties are interesting in the light of electronic and photonic properties.

In this report, we will introduce a unique approach of forming complementary coordination dimer and its developments towards various directions not only to linear one-dimensional but two-dimensional ring or planar array formation. The functional development covers also antenna function for artificial photosynthesis, and further materials having huge third order nonlinearities or extremely large cross sections of two photon excitation.[3,4]

2. RESULT AND DISCUSSION

2.1 Special pair arrangement

We have analyzed the X-ray crystallography of bacterial reaction center carefully how special pair is arranged by using supramolecular strategy. Two bacteriochlorophylls are coordinated by imidazolyl substituents of histidine in the transmembrane helices. When this coordination structure is rotated 180° along the axis of chlorophyll for chlorophyll-imidazolyl coordination pair, two imidazolyl substituents could be connected directly to the counterpart chlorophyll rather than the original peptide matrix support. It was anticipated that the

complementary nature of coordination must stabilize the coordination bonds significantly.[5]

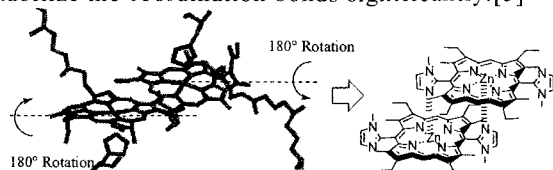


Fig. 1 Principle of structure formation by complementary coordination inspired by special pair motif in nature.

According to this idea, *meso-N*-methylimidazolyl-substituted porphyrin was synthesized. Insertion of Zn metal gave a dramatic change on the UV/visible absorption spectrum. Soret band split into two bands of almost equal intensities at 408 and 430 nm. The large splitting was accounted for by blue and red shifts by exciton interactions of face-to-face and head-to-tail transition dipoles, respectively. ^1H NMR spectrum also showed a characteristic shift behavior in a way that a half of the porphyrin ring was up-field shifted by the strong ring current effect of the facing porphyrin. Since the central Zn(II) ion in the porphyrin framework accepts only one axial coordination, no further coordination can proceed. Therefore, the species existing in the solution was almost 100 % dimer even in dilute solution such as 10^{-9} M, since the stability constant was estimated as large as 10^{10} M^{-1} in chloroform.[6]

2.2. One dimensional linear array

Coupling of this complementary coordination set, porphyrin-imidazole-Zn **1**, at the *meso* position gave bis(imidazolylporphyrinatoZn(II)) **3**. By the continuation of complementary coordination independently at each imidazolylporphyrinatoZn unit, linear multi-porphyrin array **4** with orthogonal orientation of two π -orbital planes of **3** was obtained.[7]

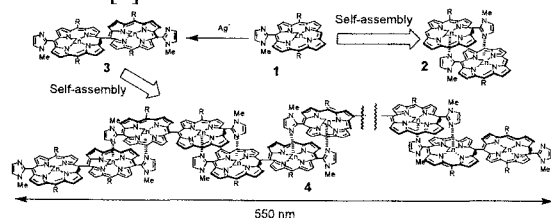


Fig. 2 Linear array structure of *meso-meso* linked bisporphyrin

In order to estimate the molecular weight, **4** in chloroform solution was analyzed by gel permeation chromatography (GPC). The elution started early at the exclusion limit of 5×10^5 and the maximum distribution appeared at 1×10^5 on the basis of polystyrene standards. Even at such a low concentration of 10^{-5} M, extremely large porphyrin arrays of up to 400 bis(imidazolylporphyrin) units with a peak maximum at 80 were linked simply by imidazolyl-Zn coordination. In accord with this estimation, AFM analysis showed linear arrays of a few hundreds to thousand nm lengths. It may be

worthwhile to comment here that the fluorescence quantum yields of **2** and **4** in benzene solution were estimated as 0.043 and 0.053, respectively. In the sense of light harvesting, it is interesting that the fluorescence intensity of **4** with a long array structure is not lost at all, but even higher than that of **2**.

The absorption spectrum of *meso-meso* coupled dimer species were split into two peaks at 415 and 453 nm for free base of **3** and 410 and 492 nm for Zn complex **4**. The longer Soret band results from continuation of head-to-tail exciton interaction and is most sensitive to the degree of coordination length. When the concentration effect on the degree of organization was examined in a range 5.0×10^{-9} - 2.2×10^{-4} M, the longer Soret band remained constant at 492 nm to show the maintenance of the long array structure even at the lowest limit.

Although the coordinate bond is strong enough to keep the array structure, addition of coordinating solvents changed the structure easily. This methodology of coordination bond breaking can be used for the structure control. A mixture of **2** and **4** was dissolved in a chloroform-methanol (1:1) solution, followed by evaporation, to destroy and reconstitute the array structure, respectively. GPC analysis of the sample after this reorganization procedure gave many intermediate peaks between **2** and **4** (Fig. 3). The peak at the longest retention time corresponded to **2** and peaks at shorter retention times was assigned after isolation as a series of compounds having different *n*, *n* being the number of units of **3** intervened between **1** terminals. The result demonstrates that the once formed coordination structure can be broken by the addition of coordination solvents and reconstructed by eliminating such the solvent. It means also that we can terminate the molecular array by the addition of appropriate terminator, whose examples will be demonstrated in the later section.

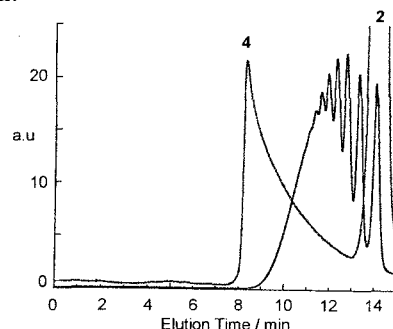


Fig. 3 GPC elution curve before and after reorganization by the addition of MeOH.

2.3 Two dimensional array

Linear array structure of porphyrin may be an interesting molecular materials for electronic/photonic application. In these cases, however, the formation of only one defect in the molecule cuts off the total conduction. In the light of this safety consideration, propagation of

the array structure in two-dimensions is desirable, because coordination network will not disrupt the conduction even if defects were involved. According to this concept, a porphyrin pentamer **5** was designed so that four imidazolylporphyrinatoZn's attached to the central porphyrin might afford complementary coordination at each site to produce a two-dimensional network of porphyrins (Fig. 4). [8]

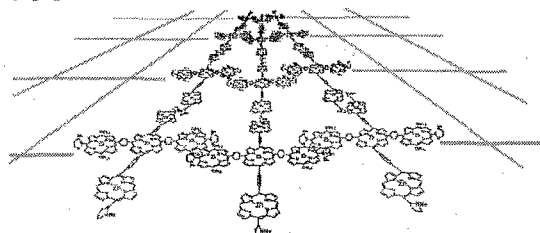


Fig. 4 Coordination network of multi-porphyrins.

Two dimensional organization, however, gave immediately insoluble materials in any solvents tested. Therefore a higher degree of organization was effected by using a reorganization procedure, where the monomeric species was first prepared in pyridine, which disturbed the complementary coordination, and then pyridine was eliminated gradually to obtain a thin film. AFM image demonstrated development of large area over 390 nm with a thin layer structure of 2.0 ~ 2.4 nm, i.e., 6 ~ 7 porphyrin layers. The length of two-dimensional network corresponds to the link of around 130 porphyrin pentamer units.

Fig. 5 shows the fluorescence mapping image (5a) of the film by use of a scanning confocal microscope and the fluorescence spectrum (5b) of the film at the point indicated by the arrow. The coincidence of two images suggests that the porphyrin array develops two dimensionally with molecular lengths reaching over a 100 ~ 200 nm scale.

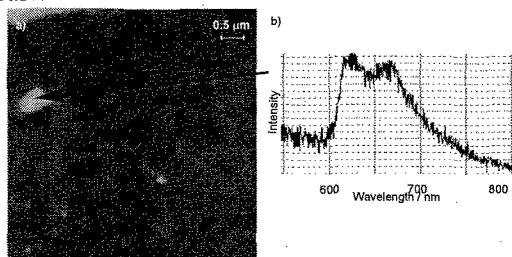


Fig. 5 Image of confocal microscope (a) and its fluorescence spectrum (b). (Reprinted with permission from ref.8. Copyright 2003 American Chemical Society)

2.4 Macrocylic antenna complex

Meso-meso linked bisporphyrin gave a giant porphyrin array as a result of large stability constant of complementary coordination of the imidazolyl-porphyrin-Zn set. In this case, however, the direction of coordination was restricted to be 180° to force the linear array structure. When the angle connecting two porphyrins is changed from 180° to 120°, a

drastic change of the structure is expected to give hopefully a closed ring structure with a strain-free hexamer (Fig. 6).

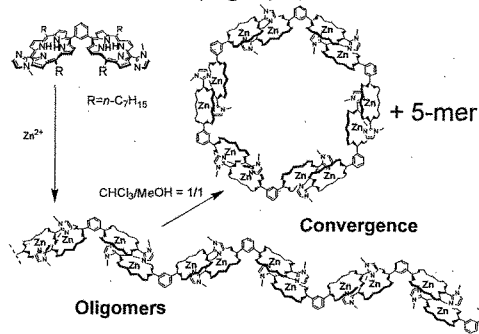


Fig. 6 Macroring formation from *meta*-phenylene bridged bisporphyrin over linear oligomers.

According to this idea, two imidazolylporphyrin's were linked with a 1,3-phenylene spacer. Zinc insertion automatically afforded a mixture of coordination assembled porphyrins oligomers having broad molecular weight distributions [9]. It is noteworthy, however, that the mean molecular size was significantly smaller than that from *meso-meso* coupled bisporphyrin as seen in the GPC (Fig. 7). Furthermore, the GPC elution curve showed a distinct spike at A corresponding to the molecular weight of the putative hexameric macroring. It is suspected that the terminal imidazolyl tends to find the zinc porphyrin counterpart at the other chain end leading to intramolecular cyclization rather than keeping the molecular terminals open for giving zig-zag chain elongation.

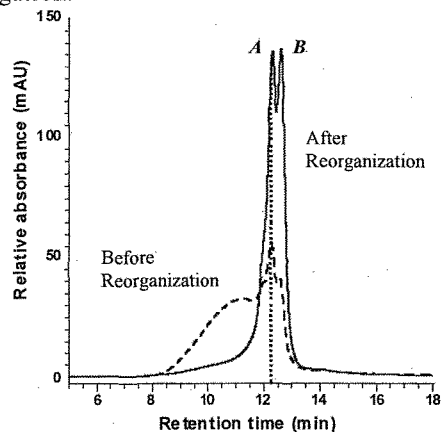


Fig. 7 GPC elution curve before and after reorganization procedures (Reprinted with permission from ref.9. Copyright 2003 American Chemical Society)

If this analysis is true, it seemed possible to control the assembly structure. Macroring structure must be favored under high-dilution conditions over linear oligomer, because the last critical step for macrocyclization must be intramolecular reaction. Therefore the once formed assembly was dissociated by the addition of MeOH and diluted by CHCl₃, followed by evaporation of MeOH to reorganize the structure again. After the treatment, the GPC

chromatogram changed dramatically, since the oligomeric components with higher molecular weights were almost completely disappeared and converged into only two peaks, one of which was the spiked peak *A* already observed initially. Two peaks *A* and *B* were easily separated by preparative GPC and the structure was analyzed by use of small angle X-ray scattering in solution and confirmed by AFM and STM as well. The peaks *A* and *B* were identified as macrocyclic hexamer and pentamer, respectively.

It is interesting to speculate the reorganization process. Macrocyclic hexamer *A* should be the most stable form without structural strain on cyclization. It has already been formed even under concentrated conditions. Under high-dilution condition, even the smaller linear pentamer tried to find the counterpart in the molecule by sharing the strain into five units. The macrocyclic ring formation must be kinetic controlled, since the formation of macrocyclic heptamer with presumably similar strain energy as pentamer could not be found in the GPC chromatogram.

The natural light-harvesting complex can be reconstituted by assembling dimeric chlorophyll subunits. By this procedure the fluorescence intensity is decreased to around a half. The fluorescence quantum yield of hexamer was similar to this value as 0.51 relative to that of the monomeric bis-zinc gable-porphyrin. The use of Zn-imidazol coordination keeps the excitation energy well as singlet. Detailed analysis elucidating the mechanism of excitation energy transfer along the porphyrin macroring or energy transfer to charge separating unit must be an exciting target in future.

2.5 Antenna effect on photocurrent generation

Recently, various approaches of artificial photosynthesis have been developed by using self-assembled monolayer (SAM) of porphyrins on solid surface. However, SAM is composed of a single molecular layer and limits the efficient absorption of light energy and therefore, highly porous surface must be employed for the achievement of efficient photocurrent generation in these cases. This situation could be improved dramatically if accumulation of porphyrins on the surface becomes possible to facilitate the light harvesting in a way similar to the natural photosynthetic system, where a large number of chlorophylls are arranged around the reaction center solely for the capture of light energy.

Thiol group is well known to modify gold surface to produce stable S-Au bonds. Therefore, imidazolylporphyrin SAM was prepared on gold surface by appending a thiol-containing meso substituent. Introduction of Zn in this porphyrin center enabled the stepwise growth of bis(imidazolyl porphyrinato)Zn array starting from this porphyrin SAM by applying the principle of coordination organization of imidazolyl-porphyrin-Zn. This was accomplished

simply by dipping the solid substrate in the porphyrin solution (Fig. 8a). UV/vis spectra after each dipping procedure demonstrated the increase of light absorption in the range of 350~750 nm depending on the dipping cycles (8b). [10]

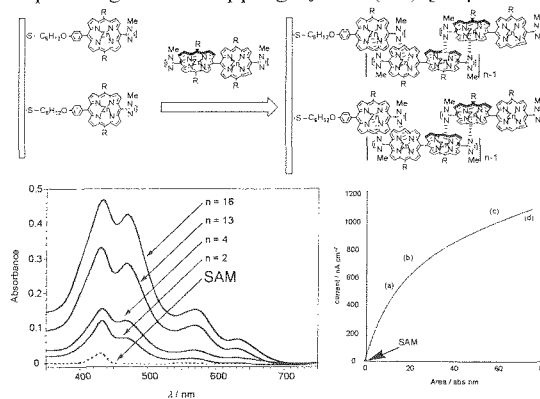


Fig. 8 Successive growth of porphyrin array and photocurrents generated. (Reproduced by permission of the Royal Society of Chemistry)

The multi-layered electrode thus obtained was irradiated in the presence of viologen in solution and the photocurrent obtained were plotted against the absorption area ($A\lambda$) integrated over the range of 350 ~ 750 nm in Fig. 8c. It is clear that the photocurrent density increased almost linearly with the increase of the absorption area in the range 0 ~ 20 $A\lambda$ and tended to saturate at higher $A\lambda$ values. This increase certainly came from the improved efficiency in absorbing light energy. Considering the photocurrent generation mechanism described below (Fig. 9), at the same time, it suggests that the excitation energy transfer along the coordination organized multi-porphyrin array must be efficient and further, the hole transfer along the chains must be efficient to maintain the efficiency. [11]

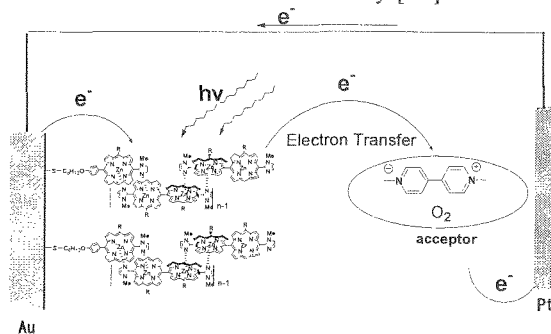


Fig. 9 Scheme of photocurrent generation

2.6 Nonlinear optics materials

Third-order nonlinear optical (NLO) materials are interesting in view of potential applications to photonic processes such as ultrafast optical switching and integrated optics. Out of several potentialities, organic material is characterized most typically by ultrafast kinetics. However, the absolute magnitude of nonlinearities is small compared with inorganic or semiconducting materials. Therefore, the increase of nonlinearities by two orders of magnitude is the

current target for leading to the real application. The present situation was summarized in Fig. 10.

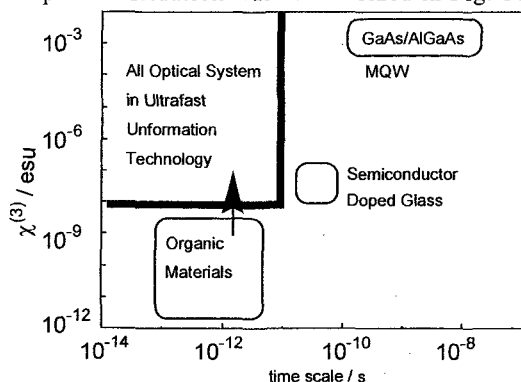


Fig. 10 Present technological status of NLO materials.

Although the general principle for obtaining large nonlinearity is not established yet, the following considerations are considered useful as a working hypothesis:

- 1) The central core part may better be composed of π -conjugating system.
- 2) The longer core length is better.
- 3) Donor and/or acceptor may be attached at molecular terminals to facilitate the intramolecular polarization.

In order to satisfy the above principles and to evaluate each factor, linear porphyrin arrays with different molecular lengths were tried to be terminated. Two terminator molecules, monoimidazolylporphyrinatoZn and monozinc complex of bis(imidazolylporphyrin) were employed and the molecular length was adjusted by the reorganization methodology already introduced in the present coordination organization technology. The compounds synthesized were shown in Fig. 11 along with the values from optical Kerr effect (OKE) measurement with 150 fs pulse laser. The irradiation was performed at 800 nm, where no absorption arises, therefore under off-resonant absorption conditions.[13]

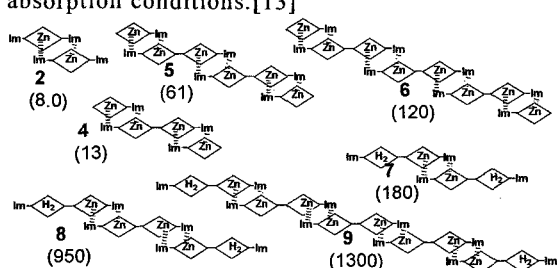


Fig. 11 Compounds and OKE values obtained.

The polarizability values $|\gamma_{yyyy}|$ of oligomers 9 ~ 11 terminated with Znporphyrin were in the range from 10^{-31} to 10^{-30} esu, while the $|\gamma_{yyyy}|$ of the series of compounds 13 ~ 14 terminated with free base porphyrin were one order magnitude larger ranging from 10^{-30} to 10^{-29} esu. The large enhancements of the $|\gamma_{yyyy}|$ values certainly originated from the attachment of free base porphyrins at the molecular terminals. The terminal free base porphyrin should behave as an

energy acceptor with respect to the central array of zinc porphyrin judging from their redox potentials, therefore stabilizing the contribution of polarized structure in the molecule. The dimeric coordination structure must contribute significantly to these large third-order optical nonlinearities, since the $|\gamma_{yyyy}|$ values were increased as the dimeric coordination structure grows.

There are several reports on NLO materials, but direct comparison of these values are difficult, unless similar methods and conditions are employed for each evaluation. When values obtained under similar conditions to the above, i.e. employing an OKE technique with laser pulse of a fs time scale under off-resonant conditions, are compared, the properties here obtained are certainly the largest class among NLO materials from organic molecules. Furthermore, the methodology of simple coordination process may also provide facile structural modifications to lead even bigger nonlinearities.

2.7 Two photon absorbing materials

The successful introduction of NLO materials of extremely large values may suggest that the complementary coordination arrays are capable of transferring molecular polarization through the array, even if interconnected porphyrin π -orbitals are orthogonal to each other. Then if two porphyrin π -planes are brought into real conjugation, a large increase of optical nonlinearity will be expected. In order to realize the idea, two porphyrins were connected by a butadiyne unit. According to the previous principle to obtain large nonlinearities, the coordination array was terminated at both molecular ends by free base porphyrin as an acceptor.

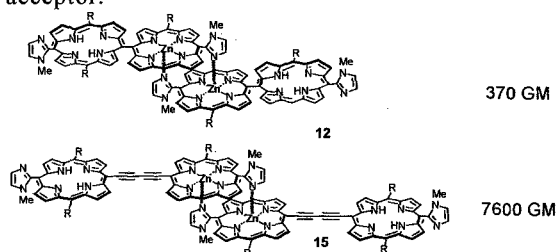
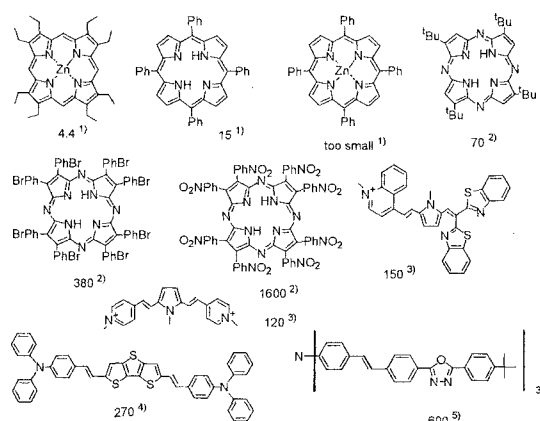


Fig. 12 Butadiyne-linked porphyrins synthesized and their $\sigma(2)$ values.

The two photon absorption (2PA) spectra were measured by an open aperture Z-scan method at wavelengths from 817 to 1282 nm using a femtosecond optical parametric amplifier. The largest $\sigma(2)$ values of 12 and 13 were 370 GM at 964 nm and 7600 GM at 887 nm (1 GM = 10^{-50} cm⁴ s molecule⁻¹ photon⁻¹) (Fig. 12).[13]

These values, especially of 15 are the largest to our best knowledge among the hitherto reported by using the same method and the similar femtosecond pulse duration. In Fig. 13, comparison of $\sigma(2)$ values obtained with femtosecond pulses was schematically shown.



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Fig. 13 Comparison of $\sigma(2)$ values reported.

The largest class of $\sigma(2)$ value of conjugated bisporphyrin may be contributed from the following factors:

- 1) Extended conjugation of large porphyrin π -orbitals by butadiyne unit
- 2) Complementary coordination contributing to effective conjugation
- 3) Attachment of free base porphyrin terminals to assist the intramolecular polarization

These series of porphyrins can generate the excited triplet state from S1 state by intersystem crossing with a high quantum yield and produce singlet oxygen. Porphyrin derivatives have been successfully applied to photodynamic therapy or tumors; but one photon absorption limited the application only to the treatment of tumor on the surface. If excitation by two photon absorption becomes possible, enormous improvement will result because the light can reach to the depth of the tissue. The result presented here will disclose such a possibility.

3. SUMMARY

In this report, we have demonstrated various extensions by using complementary coordination of imidazolylporphyrinatoZn, which mimicked originally the mode of organization of special pair of the reaction center complex of

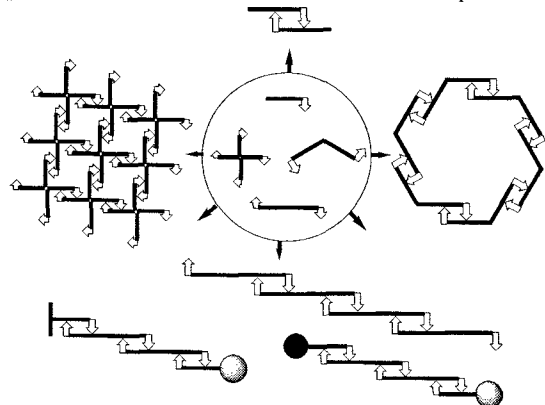


Fig. 14 Development of complementary coordination for mimicking natural system and constructing electronics and photonic materials.

photosynthetic bacteria. The same supramolecular methodology, to our surprise, has been employed to constitute the light harvesting units. Fig. 14 summarizes the development of the idea.

Coupling of imidazole-porphyrin-Zn units directly at the *meso* position extended the coordination linearly to an array of a hundreds nanometer to micrometer scale. Propagation of the array structure in four directions gave a flat film developing two-dimensions. Coupling of two units with 120° gave macrocyclic porphyrin ring converged selectively into 10 and 12 porphyrin units. The barrel structure shows close similarity with the structure and function of light harvesting complex B850 of photosynthetic bacterial. The linear array can also be regarded as a unit of effective energy/electron transferring unit. The characteristic feature of such supramolecular organization is reversible control of the structure formation and its collapse. It is easy to introduce any functional group(s) at molecular terminal(s). Therefore, the linear array was attached on gold surface by thiolate group from porphyrin. By way of antenna effect of assembled porphyrins, the efficiency of photocurrent generation was improved significantly. When electron/energy accepting groups were attached to the molecular terminals of the linear core porphyrin array, we obtained big values of second order molecular hyperpolarizability. The strategy was also very successful to obtain really big two photon absorption cross sections by using butadiyne-connected bisporphyrin.

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