PHOTO-INDUCED ELECTRON TRANSFER IN LIGHT-HARVESTING DENDRIMERS WITH WELL-CONTROLLED STRUCTURES FOR APPLICATION TO PHOTOVOLTAIC DEVICES

A Thesis

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By

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ABSTRACT

We have designed photosynthetic mimics to address the problems of charge recombination and electron transfer cascade, which occur in the artificial light-harvesting systems. To prevent backfolding, pyridine-2,6-dicarboxamides are used as the branching units to preorganize the interior of the dendron through intramolecular hydrogen bonding interactions. Multiple zinc metalloporphyrins are placed at the periphery of the dendritic structure to act as "antennae" which will efficiently absorb light to initiate an electron-transfer cascade. C$_{60}$ is placed at the focal point of the dendron to function as an electron acceptor. A unique transition metal is placed at each dendritic shell to induce unidirectional electron transfer from the periphery to the core via multiple, efficient, intramolecular ET steps.

We have synthesized dendrimers by using 2-methoxyisophthalidamide as the branching unit, 1,8:4,5-naphthalenetetracarboxydiimide (NI) as the electron acceptor and porphyrin as the electron donor. Calculations by Monte Carlo conformational search by AMBER* as the force field were carried out to find the unexpected backfolding occurred with G1 when ortho substituted phenyl groups were used as the turning units. This backfolding resulted in a sandwiched conformation. However, in the absence of this turning unit, G1 showed rigidified structure with well-separated donor and acceptor. The
dendrons were characterized by $^1$H-NMR, $^{13}$C-NMR, UV-vis, IR and MS. Photophysical studies showed that rate constant for electron transfer ($k_{ET}$) is $8.0 \times 10^8$ s$^{-1}$ and rate constant for charge recombination ($k_{CR}$) is $1.2 \times 10^8$ s$^{-1}$ for G1-l-B-Zn (97). The electronic and photonic device experiments showed that zinc porphyrin instead of free-base porphyrin increases the sensitivity to light, with photogenerated current increasing more than 10-fold, open circuit voltage ($V_{oc}$) increasing about 5-fold, and the conversion efficiency increasing about 100 fold.
DEDICATION

Dedicated to my parents in China, Lin Wu and Xiaomin Gu; my grandmother in China, Jingqing Liu; and my boyfriend, Xiaole Bai.
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study and to overcome the unexpected difficulty; it is also their love that gives me courage to face my future.
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LIST OF ABBREVIATIONS

br  broad (IR and NMR)
n-Bu  normal-butyl
t-Bu  tert-butyl
°C  degrees Celsius
calcd.  calculated
CDCl₃  deuterated chloroform
CH₂Cl₂  dichloromethane
δ  chemical shift in parts per million downfield from tetramethylsilane
d  doublet (spectra); day(s)
DMAP  4-(N,N-dimethylamino)pyridine
DMF  N,N-dimethylformamide
DMSO  dimethylsulfoxide
EDCI  1-(3-dimethylaminopropyl)-3-ethyl-carbodiimide hydrochloride
EET  electronic energy transfer
ES  electrospray
Et  ethyl
EtOH  ethyl alcohol
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<tr>
<td>ET</td>
<td>electron transfer</td>
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<tr>
<td>FF</td>
<td>fill factor</td>
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<tr>
<td>g</td>
<td>gram(s)</td>
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<tr>
<td>h</td>
<td>hour(s)</td>
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<tr>
<td>H or ¹H</td>
<td>proton</td>
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<tr>
<td>HOMO</td>
<td>highest occupied molecular orbit</td>
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<tr>
<td>HRMS</td>
<td>high resolution mass spectrometry</td>
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<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>ITO</td>
<td>indium tin oxide</td>
</tr>
<tr>
<td>J</td>
<td>coupling constant in Hz (NMR)</td>
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<td>J_{sc}</td>
<td>short circuit current density</td>
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<tr>
<td>k</td>
<td>kilo</td>
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<tr>
<td>L</td>
<td>liter(s)</td>
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<tr>
<td>LH</td>
<td>light-harvesting</td>
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<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbit</td>
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<tr>
<td>m</td>
<td>milli; multiplet (NMR)</td>
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<tr>
<td>μ</td>
<td>micro</td>
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<tr>
<td>M</td>
<td>moles per liter</td>
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<tr>
<td>MALDI</td>
<td>matrix assisted laser desorption ionization</td>
</tr>
<tr>
<td>Me</td>
<td>methyl</td>
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<tr>
<td>MeOH</td>
<td>methyl alcohol</td>
</tr>
<tr>
<td>MHz</td>
<td>megahertz</td>
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mol  mole(s)
MS   mass spectrometry; molecular sieves
m/z  mass to charge ratio (MS)
N    equivalents per liter
Ni   1,8:4,5-naphthalenetetracarboxydiimide
NMR  nuclear magnetic resonance
Obsd observed
p    para
Pd   palladium
Ph   phenyl
ppm  parts per million
py   pyridine
q    quartet (NMR)
QE   quantum efficiencies
RC   reaction center
rt   room temperature
s    singlet (NMR); second(s)
t    tertiary (tert)
t    triplet (NMR)
THF  tetrahydrofuran
TLC  thin layer chromatography
$V_{oc}$ open circuit voltage
ZnTPP zinc tetraphenylporphyrin
CHAPTER 1

INTRODUCTION

Designing efficient light-harvesting materials to mimic the natural photosynthesis has been of great interest in the past 20 years,\(^1\) due to the realization that we are exhausting the fossil fuels. In the past billions of years, nature has evolved an effective pathway to convert the solar energy into chemical energy in the form of ATP,\(^2\) which is the energy source of most biological activities. If we can mimic this highly efficient light-harvesting process followed by energy transfer, electron transfer and charge separation processes, not only we can reduce our dependence on the fossil fuels, we can also expect a sustainable and clean energy source.

1.1 Photosynthesis Represented by Purple Bacteria

Purple Bacteria is the most studied of all photosynthetic systems. Through the high resolution X-ray crystal structure of its photosynthetic unit, it shows that a central reaction center (RC) that is surrounded by light-harvesting (LH) complexes (Fig. 1.1).\(^3\) These LH complexes are a multichromophore array composed of chlorophyll molecules (Fig. 1.2)\(^4\) embedded in a protein matrix. These light-harvesting complexes act like an
"antenna" which absorbs wide range of solar spectrum. Meanwhile, due to the strong interaction between these pigments, exciton states delocalized over several molecules are formed upon photon absorption. Following this photoexcitation, the solar energy is funneled from the light-harvesting (LH) complexes to the nearby reaction center (RC) through electronic energy transfer with unity efficiency. Charge separation is achieved by charge transfer from the excited reaction center (RC) to quinine acceptor that ultimately results in chemical energy.

Fig. 4.1 Schematic representation of light-harvesting assembly in purple bacteria.
Fig. 1.2 Chlorophyll Molecules.$^4$

Inspired by natural photosynthesis, we can get some clues that in order to achieve long-lived charge separation, three factors are important: (1) the large spatial separation between the excited donors and the final quinone acceptor group, (2) the energetically favorable cascade mechanism that sequentially yields a lower energy charge-separated pair at each electron-transfer stage, and (3) the removal of the reduced quinone from the reaction center through a transmembrane process.

1.2 Review of Photovoltaic Effect

The term of "photovoltaic" is defined as "providing a source of electric current under the influence of light or similar radiation".$^7$
Compared with organic photovoltaic materials, their inorganic counterparts has been more studied and commercialized for years already. Although traditional inorganic semiconductor solar cells have reached the power conversion efficiency of over 20%, and inorganic/organic dye-sensitized cells of about 10%, the efficiency for pure organic semiconducting photovoltaic devices is still less than 7%. The main problems of the organic materials are poor exciton dissociation caused by tightly bound excitons (which means that photogenerated excitations are strongly bound and do not spontaneously dissociate into charge pairs), poor charge transport (actually, the limiting factor is the poor electron transport), narrow solar spectrum absorption, low red absorption, and low stability. However, organic materials are attractive because of the possibility of large-scale production, ultra thin and flexible devices, tuning the material properties by modifying the structure, etc.

In the past decade, unprecedented research progress has been made toward organic solar cells. And organic photovoltaic devices also have experienced several generations. The initial one is monolayer device, or “homojunction”, which is a layer of organic material sandwiched between two different conducting contacts. Usually the photogenerated excitons (photogenerated excitations) diffuse within the organic layer until it reaches a contact, where it may have the chance to produce the charge separated state. Since exciton diffusion lengths are shorter (typically 1–10 nm) than the thickness of the organic layer, charge separation is difficult to achieve. This factor greatly limits the quantum efficiencies (QE) (less than 1%) and power conversion efficiencies (less than 0.1%) of this type of single layer solar cells.
The second generation is called “heterojunctions”. The bi-layer device with a structure of donor-acceptor junction is a type of p/n heterojunction diode, consisting of a thin film of electron-donor molecules (p-type component) and another thin film of acceptor molecules (n-type component) sandwiched between metal contacts. This device was first reported by Tang who fabricated a two-layer cell of copper phthalocyanine and a perylene tetra-carboxylic derivative with the power conversion efficiency (the ratio of the electric power produced by a photovoltaic device to the power of the sunlight incident on the device) of about 1% and the fill factor (parameter which is a measure of the performance of solar cell in terms of generated power; corresponds to the area under the current-voltage characteristic of the cell between short-circuit current value on the current axis and open-circuit voltage value on the voltage axis; should be as close to 1 as possible) of 0.65. The limitation of this device is that only the thickness within the exciton diffusion scale is efficient, which limits the device efficiency.

In the mid 1990s, a breakthrough has been made with introduction of “bulk-heterojunction” solar cells, which were made by direct mixing of a soluble p-type conjugated polymer and C_{60}, or other fullerene derivatives, as n-type component. Compared with “heterojunctions”, this device has the advantages of effective interaction between the donor and the acceptor components within these “bulk-heterojunction” solar cells and this interaction can take place in the entire device’s volume. However, the compatible morphology between the components is still crucial to the device performance. Fig. 1.3 shows one example of the device structure of “bulk-heterojunctions” with MDMO-PPV (poly[(2-methoxy-5-(3,7-dimethyloctyloxy)-p-
phenylene) vinylene]) (Fig. 1.4) as the polymeric electron donor and PCBM (Fig. 1.4) as the electron acceptor. The quantum efficiencies (QE) of 6–8% was reported.

![Schematic representation of a "bulk-heterojunction" photovoltaic device.](image)

Fig. 1.3 Schematic representation of a “bulk-heterojunction” photovoltaic device.

![Structures of MDMO-PPV and PCBM.](image)

Fig. 1.4 Structures of MDMO-PPV and PCBM.

The electron-transfer mechanism of the donor-acceptor heterojunction can be illustrated by Fig. 1.5. First, upon photo-excitation, one photon is absorbed by the low energy gap.
material (usually the electron donor in heterojunction devices) which results in one electron in HOMO being promoted to LUMO. If the electron affinity of the acceptor is lower (low-lying LUMO) than that of the acceptor, the excited electron in LUMO of the donor will be transferred to LUMO of the acceptor, and this electron will be further removed by the cathode made of a low work function metal, such as Al, Ca or Mg. At the same time, because one electron is removed from donor’s HOMO to LUMO, a hole is produced in its HOMO. And this hole can be transported to anode, typically indium tin oxide (ITO).

Fig. 1.5 Schematic representation of electron-transfer mechanism of donor-acceptor heterojunction. (1. a photon absorption; 2. charge separation; 3. hole-transport; 4. electron-transport; 5. interfacial recombination; 6. geminate recombination.)

The third generation of organic photovoltaic devices is so-called “double-cable” consisting of p-type conjugated backbones (donor-cable) bearing directly grafted or tethered acceptor groups such as fullerene moieties (acceptor-cable). The advantages of this type of device are maximized effective donor/acceptor interfacial area and the
capability to prevent phase separation and clustering phenomena. One example is illustrated in Fig. 1.6 with poly(p-phenylenevinylene) and poly(p-phenylene ethynylene) covalently linked with methanofullerene moieties. It was reported that the current voltage (I/V) curves of the device recorded in the dark and under white-light illumination (100 mW cm⁻²) revealed a short circuit current density (Jsc) of 0.42 mA cm⁻², a open circuit voltage (Voc) of 830 mV, and a fill factor (FF) of 0.29. Concerning the fact that the fullerene loading of 31.5 wt% in this double-cable based solar cell is less than half of that (75 wt%) in “bulk-heterojunction” solar cells, its performance is already competitive.

![Poly(p-phenylenevinylene) and poly(p-phenylene ethynylene) covalently linked with methanofullerene moieties.](image)

Furthermore, Liddell et al have synthesized a dihydropyrene-porphyrin-fullerene molecular triad which exhibits photo-switchable photoinduced electron transfer (Fig. 1.7). In this molecule, a DHP-P⁺-C₆₀⁻ charge separated state is produced by photo excitation of the porphyrin moiety followed by photoinduced electron transfer. Upon
another charge transfer process, DHP\(^{-}\)-P-C\(_{60}\) is resulted, which has a lifetime of 2 \(\mu\)s and is formed in an overall yield of 94\%. The DHP moiety is photoisomerized to the cyclophanediene (CPD) when exposed to visible (\(\geq 300\) nm). At this stage, although excitation of the porphyrin moiety of CPD-P-C\(_{60}\) produces a short-lived (< 10 ns) CPD-P\(^{+}\)-C\(_{60}\) state, further charge shift to the CPD moiety does not occur. Long-lived charge separation is not observed. Irradiation of CPD-P-C\(_{60}\) with UV (254 nm) light converts the triad back to the DHP-P-C\(_{60}\) form.

![Diagram](Image)

**Fig. 1.7** Photo-switchable photoinduced electron transfer in a dihydropyrene-porphyrin-fullerene molecular triad.
1.3 Light-Harvesting Dendrimers

From above discussion, it is clear that although small molecular or polymeric photovoltaic systems can reproduce part of the natural photosynthesis, such as light-absorption, photon excitation, electron transfer or energy transfer, there are still many inherent limitations. First, due to the limited number of light-harvesting chromophores that can be grafted, efficient and broad wavelength absorption are hard to achieve, which makes the power conversion efficiency relatively low. Secondly, although placing the donor and acceptor close to each other can increase the efficiency of electron transfer or energy transfer, it also opens up the opportunity for charge recombination.

Nature has already evolved proven effective structures to transform solar energy into chemical energy. However, small molecular or polymeric photovoltaic systems are not “exactly” mimicking it. In natural photosynthetic systems, the reaction center is surrounded by an array of closely interacting light-harvest chromophores, which act like “antenna”; and there is spatial separation between excited chromophores and the acceptor quinine, which prolongs lifetime of charge separated state.

In order to mimic natural process, dendrimers are apparently structurally more effective. Dendrimers are well-defined, tree-like macromolecules.\textsuperscript{13} With peripheral units, a core, and intervening branching units, dendrimers have perfect scaffolds for light harvesting applications.\textsuperscript{2} Usually the light absorbing chromophores are placed at periphery and core functions as an acceptor. The number of peripheral chromophores increases from lower
generation to higher generation, from which artificial “antenna effect” can be expected. Through the unique structure endowed from the branching units, the absorbed energy or excited electron can be funneled to the focal core. (Fig. 1.8³)

![Diagram of Dendron and Dendrimer](image)

Fig. 1.8 Schematic diagram of the structure of a dendron and a dendrimer.

There are mainly two mechanisms for light-harvesting dendrimers. First one is electronic energy transfer (EET). (Fig. 1.9) It starts from excitation of the donor usually with larger band gap to cause one electron promoted to LUMO. In the presence of some energy funnel mechanisms (*vide infra*), this exciton can be quenched by energy transfer to the acceptor with small band gap. If the periphery of dendrimer is decorated with these light-harvesting donors and the low energy gap acceptor is placed at the core, this architecture exactly reproduces the energy transfer process in natural photosynthesis.
Fig. 1.9 Electronic energy transfer (EET) mechanism.\textsuperscript{13}

In the energy transfer process, usually the fluorescence of the donor is quenched. Consequently, when the donor is excited, only the fluorescence of the acceptor is observed.

The second mechanism is electron transfer (ET). (Fig. 1.10) Photo excitation also promotes one electron of donor from HOMO to LUMO, however in the following step, this excited electron is transferred to the LUMO of the acceptor. At this stage, there is a positive charge on donor and negative charge on acceptor, which is call “charge separated state”. Charge recombination will compete with this charge separation. In dendritic
structure, well separated donor and acceptor (if no back-folding) can diminish charge recombination, which contributes to the long-lived charge separated state. As in energy transfer process, fluorescence of the donor is also quenched, but no fluorescence of acceptor will be observed.

Fig. 1.10 Electron transfer (ET) mechanism.

It must be pointed out that sometimes both electron transfer and energy transfer can happen to the same dendrimer. One example is presented by Thomas et al. They synthesized a bifunctional non-conjugated dendrimer (Fig. 1.11) with diarylaminopyrene units at the periphery as energy and electron donors, a benzthiadiazole moiety at the core as energy and electron acceptor and benzyl ether as backbone. They found the energy transfer which occurs on a picosecond time scale with efficiency of 80% to 90% takes place from the periphery to the core. This is followed by the charge-transfer process which occurs on a nanosecond time scale with efficiency of 70% to 80% from the core to the periphery.
Energy transfer can proceed by either through-bond mechanism (Dexter type) or through-space mechanism (Förster type).\textsuperscript{1,3,13} "Through-bond" interaction is defined as the electronic coupling between the donor and the acceptor involving the participation of the wave functions of the spacer molecules.\textsuperscript{1} This interaction diminishes exponentially with distance ($e^{-r}$).\textsuperscript{3,13} Rigidity and conjugation are the key parameters and the bridging moiety plays a crucial role in this Dexter energy transfer.\textsuperscript{3} "Through-space" interaction is defined as the electronic coupling involving only direct overlap of the wave functions of the donor with those of the acceptor.\textsuperscript{1} This interaction is proportional to the reciprocal of $r^6$.\textsuperscript{13} Dipole–dipole interaction is important. And the properties of the chromophores, such as transition dipole moments, spectral overlap of donor emission and acceptor absorption, as well as the interchromophoric distance, play an important role in Förster energy transfer.\textsuperscript{3}
Overall, spectral overlap between donor emission and acceptor absorption is favored for both energy transfer mechanisms.  

Back folding is a big issue in some dendrimers with flexible scaffold. Due to the overcrowded periphery in the dendritic architecture, it is quite natural for it to back fold the branches toward the core. However, conformational mobility caused by flexible branches often leads to undesired chromophore interactions such as aggregation, excimer formation, and dye self-quenching. Dendrimers with relatively rigid structure caused by hydrogen-bonding, ionic interaction or conjugation, may overcome most of the limitations occurring in otherwise structurally flexible dendrimers.

On the other hand, energy gradient is also important for effective energy transfer. It has been proved that stepwise energy transfer following the energy gradient is favored compared with the direct energy transfer from the donor to the acceptor.

A triad synthesized by Weil et al addressed both the problem of back folding and cascade energy transfer. (Fig. 1.12) This triad is composed of three chromophores, terylene tetracarboxdiimide, perylene dicarboxmonoimide and naphthalene dicarboxmonoimide. First, due to the rigidity rendered by polyphenylene, this dendrimer shows no interaction between the chromophores. Secondly, when naphthalene dicarboxmonoimide moiety is excited, strong fluorescence from terylene tetracarboxdiimide is observed, although there is no spectral overlap between naphthalene dicarboxmonoimide emission (431 nm) and terylene tetracarboxdiimide
absorption (665 nm). This phenomenon is explained by a cascade energy transfer from naphthalene dicarboxmonoimide to perylene dicarboxmonoimide, then further to terrylene tetracarboxdiimide. Interestingly, fluorescence from terrylene tetracarboxdiimide is strongest when naphthalene dicarboxmonoimide moiety is excited, followed by that when perylene dicarboxmonoimide moiety is excited, while excitation of terrylene tetracarboxdiimide itself results weakest intensity of fluorescence. Then, we may conclude that the intensity of a sensitized emission is stronger than that of a direct-core emission, that is, sensitization of the chromophore by a large light-harvesting antenna is more efficient than direct excitation at the absorption maximum by an external light source.

Fig. 1.12 A triad with rigid structure and showing cascade energy transfer.
CHAPTER 2

RESULTS AND DISCUSSION

2.1 Design Background

Dendrimers apparently have the ideal architecture for light harvesting. However, the previous studies show that there are still several challenges. First one is backfolding exhibited by flexible dendrimers. This flexibility creates a tendency of the terminal groups to backfold toward the central core, in order to relieve steric congestion at the dendrimer surface. Thus, the terminal groups are close to the core, which provides a mechanism for rapid through-space charge recombination. The second problem is the difficulty to achieve the stepwise electron transfer which has already been proven to be more efficient than direct electron transfer from the donor to the acceptor. On the other hand, both well-controlled dendritic structure and cascade electron transfer can contribute to the better charge separation.
2.1.1 Initial Design

In order to overcome the problem of backfolding, dendrons with well-defined secondary structure, controlled by hydrogen-bonding or metal coordination, will be employed to increase electron transfer rates and reduce through-space charge recombination by maintaining the spatial remoteness of the electron donor and acceptor. It has been demonstrated that 4-amino-pyridine-2,6-dicarboxamide as the branching AB$_2$ unit can be used to preorganize the interior of the dendrons through intramolecular hydrogen bonding interactions.$^{15}$ Pyridine-2,6-dicarboxamide derivatives have three possible conformations with syn-syn conformation being the most stable one.(Fig. 2.1)$^{16}$ In the syn-syn conformation, two amide NH groups are oriented in close proximity to the pyridine-N due to intramolecular N-H hydrogen bonding as well as repulsive electrostatic interactions between the amide oxygens. These interactions force the terminal R groups to be positioned at the periphery of the dendron thereby precluding backfolding. Depending on the bulkiness of R groups, an overall helical conformation (P or M helix) can be formed.

![Conformational equilibria of pyridine-2,6-dicarboxamides](image)

Fig. 2.1 Conformational equilibria of pyridine-2,6-dicarboxamides favors syn-syn conformation.$^{16}$
Based on our previous work, there are two general classes of folded dendron structures (Type I and II, Fig. 2.2).\textsuperscript{17} Type I dendrons are constructed using 4-aminopyridine-2,6-dicarboxamide as the repeating unit throughout the structure, in which the hydrogen bonds restrict the backfolding of the branches of each monodendron.\textsuperscript{17,18} Furthermore, by using tetraphenyl porphyrin molecules as the terminal groups, the $\pi$-$\pi$ stacking interaction will tend to put these terminal groups close to each other, which also restrict backfolding. Consequently, a propeller-like conformation is expected. For the purpose of a more compact structure, type II dendrons are designed to incorporate a 2-aminobenzamide turning unit at each generational shell.\textsuperscript{17,18} This modification induces the dendrons to fold into a tightly packed conformation. By time-resolved fluorescence anisotropy studies (TRFA), it was demonstrated that the hydrodynamic volume of II-G2 was smaller than for I-G2, although II-G2 has greater molecular weight.\textsuperscript{19} This means that II-G2 has a more compact conformation. And the stability of helical secondary structure was also dramatically enhanced.\textsuperscript{19}

Fig. 2.2 Schematic Depiction of Type I and Type II dendrons.\textsuperscript{17}
In order to address the second issue of electron transfer cascade, a unique metal is designed to be incorporated at each generational shell; multiple zinc metalloporphyrins are to be placed at the periphery of the dendritic structures; C\textsubscript{60} will be placed at the focal point of the dendrons to function as an electron acceptor. Multiple zinc metalloporphyrins efficiently absorb light in a fashion similar to the "antennae" in purple bacteria and initiate an electron-transfer cascade, and it will also serve as electron donors. Fullerene C\textsubscript{60} is known to have an extraordinarily small reorganization energies (\lambda) for electron-transfer, which results both from the delocalization of \pi-electrons over a three-dimensional surface and the rigidity of the aromatic \pi-sphere.\textsuperscript{20,21} This dendritic structure creates an energy gradient proceeding from the periphery porphyrins to the focal fullerene. The metal center will serve to create an exergonic electron transfer cascade resulting in long distance charge separation. This arrangement of metal centers will also slow charge recombination by making the reverse electron transfer endergonic.
Energy levels involving the periphery, metal-bridging groups and the core were determined to calculate the energy evolved from each electron transfer step. In order for such a cascade mechanism to be effective, upon irradiation, the reduction potentials \(E_{\text{red}}\) of the metal dendrons must yield rate constants (through properly tuned free energies) that compete with electron-transfer directly from the porphyrin to the \(C_{60}\) unit. We have determined the redox potentials of model G1-Ni-dendron and G1-Cu-dendron by cyclic voltammetry$^{42}$ to find: $E_{\text{ox}}$ (Cu-dendron) 1.32 V, $E_{\text{red}}$ (Cu-dendron) -1.05 V; $E_{\text{ox}}$ (Ni-dendron) 0.890 V, $E_{\text{red}}$ (Ni-dendron) -1.25 V, vs. SCE. Using the known one-electron reduction potential for
monosubstituted C_{60}\textsuperscript{22} ranging from -0.3 V to -0.4 V (vs. SCE); excited energy for zinc tetraphenylporphyrin (ZnTPP), E_{S^*} = 2.10 eV and its oxidation potential of about 0.8 V\textsuperscript{23} along with the equation: \( \Delta G_{ET} = E(D^{+}/D) - E(A/A^-) - ES^* \), the approximate free energies can be resulted as shown in Fig. 2.5.

![M = Ni G1-Ni-dendron](image)

![M = Cu G1-Cu-dendron](image)

Fig. 2.4 G1-Ni-dendron and G1-Cu-dendron.

![Fig. 2.5 Schematic drawing of the relative energy levels and (possible) sequence of electron- and energy-transfer events occurring in metallated G2 after irradiation. The dendritic branches are indicated as metal-bridging groups (M\textsuperscript{III}B), where M represents the appropriate metal (Cu or Ni) and B represents the dendron itself.](image)
2.1.2 Second Design

Due to the expected complexity and difficulty encountered in the synthesis of fullerene C_{60} based dendrimers with 4-aminopyridine-2,6-dicarboxamide as branching unit, 1,8:4,5-naphthalenetetracarboxyliumide (NI) was used as the electron acceptor and 2-methoxyisophthalidamide as the branching unit, (Fig. 2.6) for a preliminary study. X-ray crystallography, DFT calculations and NOESY spectroscopic analysis demonstrated that this branching unit exists predominantly in the syn-syn conformation similar to the pyridine 2,6-dicarboxamides.\textsuperscript{43} Monte Carlo conformational searching suggests that this conformational preference folds the dendron in a manner that stacks the porphyrin chromophores with an interchromophore distance of ca. 4 Å (conformation will be provided later), however this packing is not optimized. These chromophores serve as electron donors by undergoing photoinduced electron transfer upon irradiation.

Fig. 2.6 Second design of G1 dendrimers of type I and type II.
2.2 Synthesis and Characterization

2.2.1 Synthesis and Characterization of Dendrimers with C₆₀ as the Core and 4-Amino-Pyridine-2,6-Dicarboxamide as the Branching Units

Key: (a) 60 °C, then 100 °C, 18%; (b) paraformaldehyde, C₆₀, toluene, reflux for 2 h, 9.0%; (c) NaOH, H₂O, EtOH, then HCl.

Scheme 2.1 Synthesis of fulleropyrrolidine derivative 7.²⁴,²⁵

N-(p-Carbethoxyphenyl)glycine (3) was synthesized following the procedure by Nair.²⁴ 1,3-Dipolar cycloaddition of the azomethine ylide generated by condensation of the N-(p-Carbethoxyphenyl)glycine (3) with formaldehyde generated in situ by heating paraformaldehyde to C₆₀ led to fulleropyrrolidine derivative (6). This compound has exceptionally low solubility in almost all the organic solvent except CS₂. Hydrolysis of this ethyl ester under common basic condition resulted in insoluble red stuff. It was noted that the fullerene could be attacked by hydroxide by nucleophilic addition.²⁶
Key: (a) toluene, reflux for 5 h, 12%; (b) NaH, toluene, 60 °C for 3 h, then methanol.

Scheme 2.2 Another hydrolysis condition for fulleropyrrolidine derived ester.\textsuperscript{26,27}

In order to improve the solubility of fulleropyrrolidine derivative, paraformaldehyde was replaced by octyl aldehyde. However, it appeared that reactivity of octyl aldehyde was much less than that of paraformaldehyde. The longer reaction time was needed. The long chain attached to fullerene greatly improved the solubility, and the compound 19 can dissolve in normal solvents, such as toluene, dichloromethane, chloroform, etc. \textsuperscript{1}H-NMR shows a lot of impurity peaks around 0 ppm – 2 ppm. It was caused by some impurities attached to C\textsubscript{60} because of its large aromatic system. These impurities could not be removed by flash chromatography. We used the reported method\textsuperscript{25} of precipitation by toluene/hexanes to purify the compound and the product resulted with high purity.

In the following hydrolysis step, according to the papers reported by Lamparth et al.,\textsuperscript{26,27} Sodium hydride was put in the toluene solution with fulleropyrrolidine derived ethyl ester
19. After stirred at 60 °C for 3 h, a homogeneous solution was resulted. But at this point, it was proposed that compound 19 was unaffected. Transformation to acid was accompanied by a gas evolution caused by addition of methanol. However, in contrast to the fact stated in these papers, in our reaction, instead of the desired acid as the product, this unusual hydrolysis condition seemed to transform the acid to methyl ester.

![Chemical structure](image)

Key: (a) 0.2 M LiOH, EtOH, THF; (b) toluene, reflux, 14 h.

Scheme 2.3 Another method to prepare fulleropyrrolidine based acid.

Since the ethyl group of fulleropyrrolidine based ethyl ester is difficult to remove, \(N-(p\text{-Carbethoxyphenyl})\)glycine (3) was hydrolyzed first. However, when the resultant 4-(carboxymethylamino)benzoic acid was refluxed with \(C_{60}\) and octyl aldehyde in toluene for 14 h, no reaction took place at all.
Key: (a) ethanol, rt, 2 h; (b) C\textsubscript{60}, chlorobenzene, reflux for 12 h, 28%; (c) dichloromethane, trifluoromethansulfonic acid, rt, 30 min; (d) di-\textit{tert}-butyl 4-aminopyridine-2,6-dicarboxylate, CH\textsubscript{2}Cl\textsubscript{2}, pyridine, phosgene in toluene, 0 °C ~ rt, 4 h.

Scheme 2.4 Second method to prepare fulleropyrrolidine moiety.\textsuperscript{28,29}

It shows that fulleropyrrolidine based ethyl ester is difficult to hydrolyze under appropriate condition because of the strong electrophilic nature of C\textsubscript{60}. Then we tried to use the second method to prepare fulleropyrrolidine moiety. 3-Triphenylmethyl-5-oxazolidinone (10) and N-triphenylmethyl pyrrolidine-C\textsubscript{60} (11) were prepared according to the reported procedures.\textsuperscript{28,29} After deprotection of the triphenylmethyl group, the reaction of fulleropyrrolidine 12 with di-\textit{tert}-butyl 4-aminopyridine-2,6-dicarboxylate and phosgene did not resulted any desired product 15. This may be due to the low reactivity of amino group of di-\textit{tert}-butyl 4-aminopyridine-2,6-dicarboxylate.
Scheme 2.5 Synthesis of fulleropyrrolidine derivative 25.

A third method was tried to put a linkage with tert-butyl ester on C_{60} due to the fact that tert-butyl ester is usually easy to deprotect in acid condition. Fulleropyrrolidine derivative 22 was made by the similar procedure as 1,3-dipolar cycloaddition. After hydrolysis in CH_{2}Cl_{2}/TFA 1:1, the resultant acid was transformed to acid chloride by oxalyl chloride. Then this acid chloride reacted with di-tert-butyl 4-aminopyridine-2,6-dicarboxylate to produce desired compound 25. However, from TLC, four new spots were resulted. From 2-D TLC, each separated spot became four again. In order to verify our result, we tried another method to make compound 25. We used the acid 24 reacting with di-tert-butyl 4-aminopyridine-2,6-dicarboxylate by adding HOBT, EDC·HCl and
NMM. This method gave the exactly same four new spots on TLC and each of them also separated to four after a while.

Fig. 2.7 TLC of fulleropyrroleidine derivative 25.

From above experiment, it seemed that there are three isomers existing for compounds 25. To model these isomers, benzene ring was used to replace fullerene. By MM2, it showed that there are four diastereomers with different steric energies. And the energy difference is small. Therefore, we hypothesized that these interconverting four isomers present in 25.
Fig. 2.8 Four isomers of fulleropyrrolidine derivative 25 (energy difference were calculated by MM2).

The four isomers above are partially due to three chiral centers in the molecule. For simplicity of the structure, pentadecan-8-one was used instead of actyl aldehyde in order to eliminate one of the chiral centers. (Scheme 2.6) However, the product showed decomposition to C_{60} to a large extent. At this point, it needs to be pointed out that this kind of decomposition of the fulleropyrrolidine derivatives to C_{60} was also observed to compound 19 and 22, although to a much smaller extent.

Key: (a) toluene, reflux for 5 h.

Scheme 2.6 Synthesis of fulleropyrrolidine derivative 44.
Since we got compound 25, the step seemed to be straightforward. That is, after hydrolysis of tert-butyl ester to acid, oxalyl chloride was used to make acid chloride. This acid chloride then coupled with 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (its synthesis will be provided later) to make the target G1 (70). However, compound 70 was not obtained as expected. What we got was unknown compounds.

Key: (a) (i). CH\textsubscript{2}Cl\textsubscript{2}/TFA 1:1, rt, 12 h, (ii). (COCl)\textsubscript{2}, DMF, CH\textsubscript{2}Cl\textsubscript{2}, rt, 12 h, (iii) 5-(4-aminophenyl)-10,15,20-triphenylporphyrin, CH\textsubscript{2}Cl\textsubscript{2}, pyridine.

Scheme 2.7 Synthesis of G1 (70).

Then we decided to synthesize the dendrimer in a slightly different strategy. Making G0-NH\textsubscript{2} first, then couple it with the core. Synthesis of G0-NH\textsubscript{2} is shown in Scheme 2.8. G0-N\textsubscript{3} was made first followed by a mild reduction condition by using propane-1,3-dithiol. In \textsuperscript{1}H-NMR, the chemical shift of the two hydrogen atoms of the pyridine changes from
8.11 for G0-N₃ to 7.85 for G0-NH₂. This is due to the electron-donating nature of NH₂ group.

Key: (a) PCl₅, 125 °C, 18 h, 90%; (b) tert-BuOH, DMAP, CH₂Cl₂, pyridine, 61%; (c) NaN₃, DMF, 97%; (d) (i). CH₂Cl₂/TFA 1:1, rt, 3 h, (ii). (COCl)₂, DMF, CH₂Cl₂, rt, 2 h; (e) 5-(4-aminophenyl)-10,15,20-triphenylporphyrin, chloroform, pyridine, rt, 12 h, 65%; (f) propane-1,3-dithiol, triethylamine, chloroform, 12 h, 76%.

Scheme 2.8 Synthesis of G0-NH₂ (62).

Then we tried to synthesis G1 by coupling the core of C₆₀-acid chloride with the G0-NH₂. However, we did not get G1 as desired. Maybe this is due to the strongly deactivated NH₂ group of G0-NH₂ which is caused by electron-withdrawing effect of pyridine.
Key: (a) CH₂Cl₂/TFA 1:1, rt, 12 h; (b) (COCl)₂, DMF, CH₂Cl₂, rt, 12 h; (c) G0-NH₂ (62), pyridine, CH₂Cl₂, rt, 12 h.

Scheme 2.9 Synthesis of G1 (70).

Finally, we tried to use another approach to modify C₆₀ by reacting azides with fullerene. According to the work by Hawker,⁴¹ heating azides with C₆₀ in refluxing chlorobenzene will produce the desired product with nitrogen evolving. However, what we got was insoluble brown viscous solid which essentially could not be dissolved in any organic solvent.

Key: (a) toluene, 100 °C, 5 h.; or chlorobenzene, reflux, 24 h.

Scheme 2.10 Modification of C₆₀ by azides.⁴¹
The high temperature in refluxing chlorobenzene may have caused the loss of the tert-butyl groups. Consequently, we used toluene in 100 °C instead of refluxing chlorobenzene. After 5 h, one new spot did appear from TLC. However, this new compound disappeared after 2 days. It seems that the product 51 is not stable.

2.2.2 Synthesis and Characterization of Dendrimers with 1,8:4,5-Naphthalenetetracarboxydiimide as the Core and 2-Methoxyisophthalidamide as the Branching Unit

It seemed that we met unexpected difficulties in modification of fullerene as stated above. We found that C₆₀ derivatives are not as stable as we thought before since it always tends to decompose to C₆₀, and the speed of decomposition varies according to different modifications. What is more, although in some cases we successfully put the linkage on C₆₀ in spite of the decomposition, it was still hard to couple it with porphyrin-containing dendron in the following step, which could be due to the different reaction dynamics between modified C₆₀ and porphyrin-containing dendron which both have super-molecular size.

On the other hand, the NH₂ 4-aminopyridine-2,6-dicarboxamide has extremely low reactivity because of the electron-withdrawing effect of the pyridine ring.

Based on above difficulties, for a preliminary study we proposed to build dendrimers by using 1,8:4,5-naphthalenetetracarboxydiimide (NI) the electron acceptor and 2-methoxyisophthalidamide as the branching unit. As mentioned previously, 2-
methoxyisophthalidamide exists predominantly in the syn-syn conformation. This will allow us to study the folding structures of the dendrimers and its effect on photo-induced electron transfer.

First, we synthesized tetraphenylporphyrin (42) according to the well-developed method. Then it was mono-nitrated by using concentrated nitric acid. This method was reported by Wu et al. We also used fuming nitric acid and red fuming nitric acid. It was found that in later cases, di- and tri-nitrated phorphyrin was developed for a longer reaction time, while in the former case, in a more mild condition, only mono-nitrated porphyrin was observed. Then 5-(4-nitrophenyl)-10,15,20-triphenylporphyrin (43) was not separated from tetraphenylporphyrin (42). The mixture was used for reduction. This is because of the concern that the polarity between tetraphenylporphyrin (42) and 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (52) was much large than the polarity between tetraphenylporphyrin (42) and 5-(4-nitrophenyl)-10,15,20-triphenylporphyrin (43). In a large scale synthesis, this is very helpful for flash chromatography separation. After reduction, 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (52) was resulted and unreacted tetraphenylporphyrin (42) was recycled.
Key: (a) Propionic acid, 130 °C, 1 h. 19%; (b) concentrated HNO₃ (70%), CH₂Cl₂, 0–5°C, 3 h; (c) SnCl₂·2H₂O, EtOH, concentrated HCl solution, 65°C, 1.5 h, yield from 42 to 52: 63%.

Scheme 2.11 Synthesis of 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (52).

Then 1,8:4,5-naphthalenetetracarboxydiimide derivative – diallylic ester (90) was synthesized by reacting diallyl 5-amino-2-methoxyisophthalate (89), n-butyramine and naphthalene-1,4,5,8-tetracarboxylic dianhydride. Compound 90 was resulted in statistical competition between compound 89 and n-butyramine. It also shows that unlike 4-aminopyridine-2,6-dicarboxamide, the NH₂ of 2-methoxyisophthalidamide has sufficient reactivity. After deprotection of the allyl groups by palladium catalyst and making the diacid chloride, 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (52) was coupled with the 1,8:4,5-naphthalenetetracarboxydiimide core smoothly to produce G1-I-B (94) (Scheme 2.12). Zinc-complex of G1 was also readily synthesized from free-base G1 (Scheme 2.13). Solubility of this zinc-complex G1-I-B-Zn is much different from that of free base G1-I-B. Unlike the free base G1-I-B which is soluble in many organic solvent, such as dichloromethane and chloroform, zinc-complex G1-I-B-Zn has low
solubility in chloroform and dichloromethane, but has good solubility in THF. This may be due to its large polarity as well as the more strong π-stacking interaction between zinc porphyrins which makes the structure more compact.

Key: (a) pyridine, reflux, 22%; (b) PPh₃, Pd₂(dba)₃·CHCl₃, THF; N,N-dimethylbarbituric acid, THF, rt, 73%; (c) (i). (COCl)₂, DMF, CH₂Cl₂, rt, 1.5 h; (ii). 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (52), pyridine, DMAP, CH₂Cl₂, 12 h; 76%.

Scheme 2.12 Synthesis of G1-I-B (94).
Key: (a) Zn(OAc)$_2$·2H$_2$O, CH$_2$Cl$_2$, reflux, 4 h, 62%.

Scheme 2.13 Synthesis of G1-I-B-Zn (97).

In order to determine whether there is electronic interaction between the periphery and the core and to determine the peaks in UV-vis absorption, the core part (80) and G0-I-B-NH$_2$ (81) were synthesized with similar procedures as syntheses of compound (90) and compound (94) respectively (Scheme 2.14 and Scheme 2.15). It needs to be pointed out that G0-I-B-NO$_2$ (78) is not very stable; all characterizations need to be done right after the reaction. After several days being put aside, it degraded to an intractable compound.

Key: (a) Pyridine, reflux, 2 h, 21%.

Scheme 2.14 Synthesis of core part (80).
Key (a) (i). (COCl)$_2$, DMF, CH$_2$Cl$_2$, rt, 3 h; (ii). 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (52), pyridine, DMAP, CH$_2$Cl$_2$, 12 h; 82%; (b) SnCl$_2$·2H$_2$O, THF, 12 h, 62%.

Scheme 2.15 Synthesis of G0-I-B-NO$_2$ (78) and G0-I-B-NH$_2$ (81).

Finally, in order to get a more compact structure, a turning unit, 2-aminobenzamide, was incorporated to the dendrimer. It was expected that the dendrimer would fold into a tightly packed conformation. Meanwhile, with this tight structure, we expect to see its influence on the electron transfer and charge separation. In a convergent way, the turning unit was coupled with 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (52) first, followed by coupling to the core in a similar way as synthesis of G1-I-B (94) to give G1-II-B (100). Like G1-I-B-Zn (97), this G1-II-B (100) has low solubility in dichloromethane and chloroform, but good solubility in THF. As expected, this dendrimer with turning unit has more compact structure, which causes relatively low solubility.
Key (a) (i) (COCl)₂, DMF, CH₂Cl₂, rt, 1.5 h; (ii) 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (52), pyridine, DMAP, CH₂Cl₂, 12 h; 87%; (b) SnCl₂·2H₂O, THF, 12 h, 58%; (c) (i) (COCl)₂, DMF, CH₂Cl₂, rt, 3 h; (ii) 5-(4-(2-aminoophenylcarbamoyl)phenyl)-10,15,20-triphenylporphyrin (99), pyridine, DMAP, CH₂Cl₂, 12 h; 46%.

Scheme 2.16 Synthesis of G1-II-B (100).

2.2.3 Characterizations and Conformational Calculations

Tetraphenylporphyrin (42) and 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (52) are known compounds and our ¹H-NMR spectra match well with the reported ones. ¹H-NMR spectra of porphyrins with turning units 98 (NO₂) and 99 (NH₂) show two doublets and triplets due to the ortho substituted phenyl groups. In 98, the doublets of 1- and 4- Hs
(Fig. 2.9) are at 8.06 ppm and 7.62 ppm respectively, but they shift to 6.74 ppm and 7.64 ppm respectively when 98 was reduced to 99. Similarly, the triplets of 2- and 3-Hs in 98 (Fig. 2.9) are at 7.50 ppm and 7.67 ppm respectively, but they shift to 7.30 ppm and 6.78 ppm respectively in 99. We can see the dramatic up-field shifts of 3- and 1-Hs which are at the para and ortho positions of NO₂ and NH₂. This is due to the strong electron-withdrawing effect of NO₂ in 98 while electron-donating effect of NH₂ in 99. And the chemical shifts of hydrogens on porphyrin are essentially same for 98 and 99.

Fig. 2.9 Structures of 98 and 99.

Because of the strong electron-withdrawing effect of tetracarboxydiimide, the chemical shifts of hydrogens on both naphthalene in 80 and 90 are about 8.8 ppm as a singlet. This is because N-substituted groups are not planar with naphthalene plane which makes them electronically unrelated. The chemical shift of 1-H of butyl group (position “a” in Fig. 2.10) is 4.21 ppm for both 80 and 90, and chemical shift of hydrogens of methoxyl group
(position “b” in Fig 2.10) is 4.01 ppm for 90. The chemical shifts of these hydrogens change a lot with incorporation of porphyrins as we can see below.

![Chemical structure of 90]

Fig. 2.10 Structure of 90.

In 78 and 81, the presence of two porphyrins does not change the chemical shifts and shape appearance of hydrogens on porphyrin. The chemical shift of two hydrogens ortho to NO₂ in 78 is 9.14 ppm while it up-field shifts to about 7.74 ppm buried in porphyrin peaks in 81 (page 39), which is reasonable in terms of NH₂. Chemical shift of hydrogens of methoxyl group (similar position “b” in Fig. 2.10) is 4.45 ppm for 78 and 4.32 ppm for 81. Although this is also conceivable in terms of different electronic effect of NO₂ and NH₂, both of them are down-field shifted for 0.31 and 0.44 ppm when compared to the same methoxyl group in 90 (4.01 ppm). This could be accounted by the possible conformations for 78 and 81 in which methoxyl groups are located at the deshielding region of two porphyrin rings.

As to G1-I-B (94), G1-I-B-Zn (97) and G1-II-B (100), in ¹H-NMR spectra the porphyrin region is quite similar to that of mono porphyrin except that peaks of amino-phenyl split
in 94 and 97, and peaks of m/p-phenyl split in 100. In 100, the four hydrogens on each turning unit account for two doublets (both at about 7.75 ppm buried in porphyrin peaks) of 1- and 4- positions (refer to Fig. 2.9) and two triplets with 7.39 ppm for 2- position and 7.02 ppm for 3- position (refer to Fig. 2.9).

However, the chemical shift of aromatic hydrogens on naphthalene is up-field shifted to around 8.21 ppm for 94, 8.22 ppm for 97 and 8.19 ppm for 100, while that is 8.79 ppm in the core part 90. On the other hand, similar to dendrons 78 and 81, the chemical shifts of methoxyl hydrogens are down-field shifted to 4.54, 4.47 and 4.42 ppm for 94, 97 and 100 respectively, compared to 4.01 ppm for the core moiety 90. Another noteworthy point is that the chemical shift of 1-H of butyl group (position “a” in Fig. 2.10) is 3.88, 3.84 and 2.93 ppm for 94, 97 and 100 respectively, all of which are up-field shifted for 0.33 and 0.37 ppm for 94 and 97 and 1.28 ppm for 100 when compared to the core moiety 90 at 4.21 ppm. This evidence from 1H-NMR suggests that there are some inter- or/and intramolecular interactions in these dendrimers. In order to clarify the structures, Monte Carlo conformational search by AMBER* as the force field were used to calculate the conformations.

As seen Fig. 2.11, 2.12 and 2.13, the 2-methoxyisophthalidamide branching unit exists predominantly in the syn-syn conformation with NH groups pointing towards OCH₃ to form hydrogen bonding. In G0-I-B-NH₂ (81) and G1-I-B (94), due to the absence of the turning units, their structures are rigidified with two porphyrins pointing away from each other. However, G1-II-B (100) shows a completely different structure. The turning units
in G1-II-B (100), which were supposed to give a more compact structure by tight folding of the dendron, actually allow two porphyrins to back-folding. This back-folding is also motivated by the strong \( \pi \sim \pi \) stacking between the porphyrins and naphthalene. As seen in Fig. 2.13, the naphthalene is sandwiched between two porphyrins.

Fig 2.11 The lowest energy conformation of G0-I-B-NH\(_2\) (81) by Monte Carlo (AMBER*).
Fig 2.12 The lowest energy conformation of G1-I-B (94) by Monte Carlo (AMBER*).

Fig 2.13 The lowest energy conformation of G1-II-B (100) by Monte Carlo (AMBER*).
This conformation of 100 can well explain the observed changes of chemical shifts in $^1$H-NMR spectrum. First the chemical shift on naphthalene is up-field shifted by 0.6 ppm for 100 when compared to 8.79 ppm in the core part 90. This is because the naphthalene plane is sandwiched between two porphyrin planes so that the four hydrogens on naphthalene are located at the shielding region of the porphyrins due to field anisotropy of porphyrin. What is more, this conformation also place the 1-H of butyl group in the same shielding region of porphyrins, which results a big up-field shift by 1.28 ppm compared to the core moiety 90. To sum up, due to the small flexibility from the turning units as well as the strong $\pi \sim \pi$ stacking interaction, back-folding occurs in the conformation of G1-II-B (100), which causes a close bound sandwich structure.

The phenomenon of up-field shifts on naphthalene and 1-H of butyl group were also observed in the in $^1$H-NMR spectra of G1-I-B (94) and G1-I-B-Zn (97). In contrast to G1-II-B (100) in which 1-H of butyl group is up-field shifted by 1.28 ppm compared to the core moiety 90, the changes of G1-I-B (94) and G1-I-B-Zn (97) are only 0.33 and 0.37 ppm respectively. From calculation, G1-I-B (94) does not show the backfolding. However, we can imagine that strong $\pi \sim \pi$ stacking interaction does exist between the large aromatic planar functional groups. Therefore, we reason that there is intermolecular $\pi \sim \pi$ stacking between the naphthalene and porphyrin. Compared to the intramolecular stacking, the intermolecular ones are relatively weaker and limited by other factors, like steric hindrance, the solvent, etc.
In UV-vis spectra (provided in Appendix), for tetraphenylporphyrin (42), 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (52), 5-(4-(2-nitrophenylcarbamoyl)phenyl)-10,15,20-triphenylporphyrin (98) and 5-(4-(2-aminophenylcarbamoyl)phenyl)-10,15,20-triphenylporphyrin (99), we can see distinctive Soret band absorption (about 420 nm) and Q-band absorption at about 516 nm, 552 nm, 592 nm, 648 nm. And the UV-vis spectra of the core moiety 80 and 90 are essentially same, with three absorptions at 238 nm, 360 nm and 382 nm.

G1-I-B (94) and G1-II-B (100) show the well-defined absorptions from the overlap of porphyrin moiety and core naphthalenetetracarboxydiimide moiety. However, their Soret bands (about 420 nm) apparently broaden when compared to monoporphyrin. This originates from the exciton coupling between the porphyrins which are brought close to each other by $\pi - \pi$ interactions. This broadening Soret band is also observed in the UV-vis spectra of dendron G1-I-B-NO$_2$ and G1-I-B-NH$_2$, and is also the evidence of exciton coupling.$^{47}$

### 2.2.4 Photonic and Electronic Device Assembly Studies

Given the materials ready, photovoltaic cells were constructed by independently sandwiching the dendrons (G1-I-B 94 or G1-I-B-Zn 97) between anode and cathode electrodes. (Fig. 2.14 and Fig. 2.15) Commercial ITO (5eV work function) coated glass was employed as anode electrodes. It was patterned by chemical etching using hydrochloric acid solution followed by ultrasonic cleaning process in acetone and
distilled water. The active materials, free base G1-I-B (94) in toluene and zinc complex G1-I-B-Zn (97) in THF, were spin-cast to form a ~90 nm thick layer. Finally, aluminum (3.5 eV work function) was thermally evaporated on the active layers with 150 nm thickness to form cathode electrodes. Several devices were made in the same way, and the area of active layer was about 7~16 mm². The anode electrodes were connected to the positive terminal of the voltage source. For G1-I-B (94) it was scanned from -0.1 V to +0.5 V with step size of 5 mV. For G1-I-B-Zn (97) it was scanned from to -0.5 V to +1.5 V with step size of 5 mV. The current driven through the photovoltaic devices were measured. Monochrometer filtered output from a xenon lamp (~70W) was illuminated onto the devices. The devices were excited at the wavelengths of absorption peaks in the donor porphyrin group (414, 516, 552, 590, 646 nm). The power of illumination incident on the devices was measured by a photodiode ranging from 0.20 mW to 0.30 mW.

![Schematic structure of photovoltaic device](image1.png)

![Band structure](image2.png)

Fig. 2.14 Schematic structure of photovoltaic device (left) and band structure (right).
Fig. 2.15 Devices made by G1-I-B (94) (left) and G1-I-B-Zn (97) (right).

Fig. 2.16 and Fig. 2.17 show the current density (J) ~ voltage (V) characteristic curves for different illumination conditions of the devices made by G1-I-B (94) and G1-I-B-Zn (97). It shows that when the light source is “off”, the curves essentially pass the zero point. However, when the devices were illuminated, the J~V curves were shifted down.
Fig. 2.16 J–V characteristic curves for different illumination conditions for G1-I-B (94).
Fig. 2.17 J–V characteristic curves for different illumination conditions for G1-I-B-Zn (97).

Values of short-circuit current \( I_{sc} \) (A) were obtained from the intercepts of Y-axis and values of open-circuit voltage \( V_{oc} \) (V) were obtained from intercepts of X-axis. Then values of short-circuit current density \( J_{sc} \) (A/cm\(^2\)) were calculated by dividing values of short-circuit current \( I_{sc} \) (A) by the area of active layers (cm\(^2\)). Maximum power (W/cm\(^2\)) is the maximum value of current density \( J \) (A/cm\(^2\)) multiplied by voltage \( V \) (V) when voltage varies from 0 V to \( V_{oc} \) (V). Fill factor FF was calculated using Eqn. 2.1.

\[
FF = \frac{\text{MaximumPower}(W/cm^2)}{J_{sc}(A/cm^2) \times V_{oc}(V)}
\]

Eqn. 2.1
Input power density (W/cm²) was calculated by dividing input power (W) which was measured by a photodiode over the area of the active layer (cm²). The device efficiency was calculated by Eq. 2.2.

\[
\text{Efficiency(\%)} = \frac{\text{MaximumPower}(\text{W} / \text{cm}^2)}{\text{InputPowerDensity}(\text{W} / \text{cm}^2)} \times 100\%
\]

Eqn. 2.2

The short-circuit current density \(J_{sc}\), open-circuit voltage \(V_{oc}\), fill factor and efficiency of G1-I-B (94) and G1-I-B-Zn (97) are shown in Table 2.1. We can see from the data that incorporation of Zn into the structure increases the sensitivity to light, with photogenerated current increasing more than 10-fold and open circuit voltage \(V_{oc}\) increasing more than 5-fold. Figure 2.13 summarizes \(J_{sc}\), \(V_{oc}\), and fill factor (FF) for each wavelength of illumination studied. It is noted that for these initial devices studied the power conversion efficiency of Zn-containing dendrimer (G1-I-B-Zn 94) is two-orders of magnitude higher than the metal free system (G1-I-B 97). It is also noted that both G1-I-B (94) and G1-I-B-Zn (97) showed highest efficiency when they were irradiated into around the Q-band region of the porphyrin which directly produces \(S_1\) state.
<table>
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<tr>
<th>Wavelength (nm)</th>
<th>J_{sc}</th>
<th>Voc</th>
<th>FF</th>
<th>Efficiency (%)</th>
<th>J_{sc}</th>
<th>Voc</th>
<th>FF</th>
<th>Efficiency (%)</th>
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<td>0.243</td>
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<td>1.83E-06</td>
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<tr>
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<tr>
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<tr>
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<td>0.260</td>
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<td>0.234</td>
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<tr>
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<td></td>
<td>5.31E-09</td>
<td>0.705</td>
<td>0.266</td>
<td>4.70E-05</td>
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<td></td>
<td></td>
<td>2.75E-08</td>
<td>0.770</td>
<td>0.246</td>
<td>3.65E-04</td>
</tr>
</tbody>
</table>

Table 2.1 J_{sc}, Voc, FF and Efficiency of G1-I-B (94) and G1-I-B-Zn (97).
Fig. 2.18 $J_{sc}$, $V_{oc}$, and FF of G1-I-B (94) and G1-I-B-Zn (97).

### 2.2.5 Photophysical Studies

Preliminary photophysical results for G1-I-B (94) and G1-I-B-Zn (97) have been performed in Dr. David Modarelli’s group at the University of Akron. The absorption spectra of these compounds in DMF indicate a slight red-shift in the Soret band of the porphyrins, from 417 nm to 420 nm for G1-I-B (94) and from 426 to 428 nm for G1-I-B-Zn (97). Steady state emission yields a fluorescence quantum yield ($\Phi_f$) of 0.017 for G1-I-B-Zn (97). Compared with the fluorescence quantum yield ($\Phi_f$) of 0.033 for zinc tetraphenylporphyrin (ZnTPP), the smaller value for G1-I-B-Zn (97) could indicate...
electron transfer is either relatively efficient, the S₁ state can decay more rapidly in G1-I-B-Zn (97) than ZnTPP because of more rapid relaxation processes (i.e. internal conversion), or because the porphyrins are spatially close enough for efficient energy-hopping. Since closely packed porphyrins are found in nature-occurred light-harvesting systems, it could indicate our system may approximate both to some extent.

Femtosecond pump-probe experiments indicated two components (720 ps and 36 ps) for the decay of the first excited singlet state of zinc porphyrin in G1-I-B-Zn (97). The 36 ps decay of may result from energy-transfer between zinc porphyrin groups on G1-I-B-Zn (97). Time-resolved measurements at 610 nm, where the 1,8:4,5-naphthalenetetracarboxydiimide (NI) radical anion absorbs shows a 755 ps growth, followed by an 8.3 ns decay. The similarity between the 720 ps decay of G1-I-B-Zn (97) excited state and 755 ps growth of NI radical anion indicates this value is likely a result of electron transfer (ET). By taking the average of these two values, \( \tau_s = 738 \) ps was calculated as the lifetime of the first excited singlet state the zinc porphyrin in G1-I-B-Zn (97). Therefore, rate constant of electron transfer \( (k_{et}) \) can be calculated by Eqn. 2.3, where \( k_s \) is the reciprocal of lifetime of the first excited singlet state of ZnTPP without any electron acceptor attached to it, which is 1.8 ns. Then, \( k_{et} \) is calculated to be 8.0 * 10⁸ s⁻¹.

\[
\frac{1}{\tau_s} = k_{et} + k_s
\]

Eqn. 2.3

\[
k_{cr} = \frac{1}{\tau_a}
\]

Eqn. 2.4
From the 8.3 ns lifetime ($\tau_d$) of NI radical anion decay, the rate constant for charge recombination (CR), $k_{CR}$ can be calculated as the reciprocal of this lifetime, $1.2 \times 10^8 \text{ s}^{-1}$. The values obtained for electron transfer (ET) and charge recombination (CR) are indicative of a relatively efficient ET, and a reasonably long-lived charge separated (CS) state. However, the difference between $k_{ET}$ and $k_{CR}$ is relatively small when compared to that of a porphyrin-C$_{60}$ dyad,$^{12}$ in which $k_{ET}$ was $3.0 \times 10^{10}$ while $k_{CR}$ was $3.0 \times 10^8$. But this is just a preliminary study, and we will improve electron transfer rate by modifying the structure.

Fig. 2.19 Porphyrin-C$_{60}$ dyad.$^{12}$

2.3 Future Work

Due to our unsuccessful experience with fullerene C$_{60}$ work, we temporarily shift to the dendrimers with 1,8:4,5-naphthylenedimide as the focal acceptor to do the preliminary study of the effect of dendrimer structure on the electron transfer rate and charge
recombination rate. However, C₆₀ is no doubt a better candidate as an electron and energy acceptor. So synthesis of dendrimers by incorporating C₆₀ in the focal point and fully characterization along with photophysical and device studies will be carried out. On the other hand, we have already used 2-methoxyisophthalidamide as the branching unit. However, as discussed in the initial design, pyridine 2,6-dicarboxamide is more suitable for our project since it allows us to incorporate transition metals, such as zinc, nickel and copper, at each generational shell to promote cascade electron transfer mechanism. So in the future work, based on our results from the preliminary studies, we will return to our first design of dendritic light-harvesting system to study the folding effect on the electron transfer and charge recombination.
CHAPTER 3

EXPERIMENTAL DETAILS

General

All reagents were used as shipped unless otherwise noted. THF were dried by distillation from sodium benzophenone ketyl just prior to use. \( \text{CH}_2\text{Cl}_2, \text{CHCl}_3 \) and toluene was dried by distillation from CaH\(_2\). TLC analysis was performed using Whatman silica gel 60 F\(_{254}\) on aluminum-backed plates. Silica gel used for column chromatography was E. Merck silica gel 60 (230-400 mesh). \(^1\text{H}\) NMR spectra were recorded at 250MHz or 400 MHz and \(^{13}\text{C}\) NMR spectra at 100 MHz. IR spectroscopy was performed on a Perkin Elmer 1320 spectrometer. HRMS analysis was performed in the laboratory of Dr. Chris Hadad by either electron impact mass spectrometry to obtain \( \text{M}^+ \) data, or by cationization with sodium for \( \text{M}+\text{Na}^+ \) analysis. MALDI-TOF spectrometry was performed using a DHP matrix in THF by The Ohio State University Campus Chemical Instrumentation Center.

\( N-(p-\text{Carbethoxyphenyl})\text{glycine} \) (3).\(^{24}\) In a round-bottomed flask was placed a mixture of ethyl p-aminobenzoate (4.125 g, 25 mmol) and monobromoacetic acid (3.465 g, 25 mmol). It was heated slowly under nitrogen gas. The mixture became light yellow. When
the temperature of oil bath reached 60 °C, the mixture became orange solid. The reaction was stopped when the temperature reached 100 °C. After cooled to rt, the solid was transferred to a beaker. Distilled water (200 mL) was added. After the lumps were broken, the mixture was stirred vigorously and the pH value was adjusted to 9 with 2 N sodium hydroxide solution. Then the mixture was filtered. The filtrate was acidified to pH = 3.0 by using 1 N HCl solution. It was chilled for 8 h in the refrigerator. A lot of light yellow solid was resulted, which was filtered and dried. This solid was recrystallized by ethylacetate to result white solid (0.8765 g, 18%) as the desired product.

\(^1\)H-NMR (400 MHz, DMSO) \(\delta\) 1.26 (t, \(J = 7.3\) Hz, 3H, CH\(_3\)), 3.87 (s, 2H, CH\(_2\)), 4.20 (q, \(J = 7.0\) Hz, 2H, CH\(_2\)), 6.58 (d, \(J = 8.7\) Hz, 2H, Ar-H), 6.71 (s, 1H, NH), 7.68 (d, \(J = 8.7\) Hz, 2H, Ar-H), 12.65 (s, 1H, OH).

**Fulleropyrrolidine derivative (6).**\(^{25}\) To a solution of C\(_{60}\) (100 mg, 0.14 mmol) in toluene (130 mL) was added paraformaldehyde (20 mg, 0.67 mmol) and N-(p-Carbethoxyphenyl)glycine (3) (62.44 mg, 0.28 mmol) under nitrogen and in dark. The solution was heated to reflux for 2 h. After cooled to rt, the solvent was removed under reduced pressure. The resultant solid was retaken in toluene and purified by flash chromatography (toluene) to afford brown solid (12 mg, 9.0%). \(^1\)H-NMR (250 MHz, CS\(_2\) : CDCl\(_3\) 2:1) \(\delta\) 1.44 (t, \(J = 7.1\) Hz, 3H, CH\(_3\)), 4.36 (q, \(J = 7.1\) Hz, 2H, CH\(_2\)), 5.28 (s, 4H, pyrrolidine-H), 7.25 (d, \(J = 8.7\) Hz, 2H, Ar-H), 8.09 (d, \(J = 8.7\) Hz, 2H, Ar-H).

**Fulleropyrrolidine derivative (19).**\(^{25}\) To a solution of C\(_{60}\) (75 mg, 0.10 mmol) in toluene (45 mL) was added octyl aldehyde (78 \(\mu\)L, 0.50 mmol) and N-(p-
Carbethoxyphenyl)glycine (3) (55.8 mg, 0.25 mmol) under nitrogen and in dark. The solution was heated to reflux for 5 h. After cooled to rt, the solvent was removed under reduced pressure. The resultant solid was retaken in toluene and purified by flash chromatography (toluene) to afford brown solid. This solid was then dissolved in as small volume of toluene as possible. Then hexane was added. Brown solid was precipitated immediately. This solid was washed several times by hexane. After drying, 12.6 mg of this brown solid was resulted with yield 12%. $^1$H-NMR (250 MHz, CDCl$_3$) δ 0.86 (t, $J = 6.4$ Hz, 3H, 7-H(nheptyl)), 1.26~1.52 (m, 8H, 3, 4, 5, 6- H(nheptyl)), 1.41 (t, $J = 7.1$ Hz, 3H, CH$_3$), 1.75 (m, 2H, 2- H(nheptyl)), 2.43~2.66 (m, 2H, 1- H(nheptyl)), 4.38 (q, $J = 7.1$Hz, 2H, CH$_2$), 5.14 (d, $J = 11$ Hz, 1H, pyrrolidine-H), 5.53 (d, $J = 11$ Hz, 1H, pyrrolidine-H), 6.82 (t, $J = 6.6$ Hz, 1H, pyrrolidine-H to heptyl), 7.23 (d, $J = 8.7$ Hz, 2H, Ar-H), 8.11 (d, $J = 8.7$ Hz, 2H, Ar-H); HRMS for C$_{78}$H$_{27}$NO$_2$ (ES) (M + Na) Calcd. 1032.1934, Obsd. 1032.1881 (27.15%); (M + H) Calcd. 1010.2120, Obsd. 1010.2020 (11.94%).

3-Triphenylmethyl-5-oxazolidinone (10)$^{28}$ To a solution of 2-(tritylamino)acetic acid (0.205 g, 0.65 mmol) in ethanol (15 mL) was added aqueous formaldehyde (37%, 0.3 mL) at room temperature. The mixture was stirred at rt for 2 h. Then the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane (30 mL). This solution was dried over magnesium sulfate. Then the solvent was removed by reduced pressure. $^1$H-NMR (400 MHz, CDCl$_3$) δ 3.53 (s, 2H, CH$_2$), 5.08 (s, 2H, CH$_2$), 7.17 (m, 3H, Ar-H), 7.25 (m, 6H, Ar-H), 7.41 (m, 6H, Ar-H).
N-Triphenylmethyl pyrrolidine-C₆₀ (11)²⁹ To a solution of C₆₀ (50 mg, 0.070 mmol) in chlorobenzene (65 mL) was added 3-triphenylmethyl-5-oxazolidinone (10) (27 mg, 0.080 mmol). The solution was heated to reflux for 12 h. Then after cooled to rt, the solvent was removed in vacuo. The resultant brown solid was purified by flash chromatography (petroleum ether/toluene 8:2) to yield yellow orange solid (20 mg, 28%). ¹H-NMR (250 MHz, CS₂: CDCl₃ 2:1) δ 4.17 (s, 4H, pyrrolidine-H), 7.28 (m, 3H, Ar-H), 7.41 (m, 6H, Ar-H), 7.87 (d, J = 7.5 Hz, 6H, Ar-H).

**Fulleropyrrolidine derivative (22)³⁰** A solution of tert-butyl 2-(methylamino)acetate hydrochloride (23.3 mg, 0.13 mmol), octyl aldehyde (71 µL, 59.2 mg, 0.46 mmol) and C₆₀ (92.4 mg, 0.13 mmol) in toluene (120 mL) was heated to reflux for 1 h. After cooled to rt, the solvent was removed under reduced pressure. And the residue was purified by flash chromatography (toluene/hexanes 6:4) to yield yellow brown solid, which was then precipitated from CH₂Cl₂/ethanol to give brown solid (35 mg, 28%). ¹H-NMR (250 MHz, CDCl₃) δ 0.86 (t, J = 6.5 Hz, 3H, 7-H(nheptyl)), 1.20~1.52 (m, 17H, 3, 4, 5, 6-H(nheptyl), ¹Bu), 1.90 (m, 2H, 2- H(nheptyl)), 2.29 (m, 1H, 1-H(nheptyl)), 2.53 (m, 1H, 1-H(nheptyl)), 3.13 (s, 3H, CH₃), 5.28 (t, J = 5.6 Hz, 1H, pyrrolidine-H), 5.39 (s, 1H, pyrrolidine-H); HRMS for C₇₅H₅₉NO₂ (ES) (M + Na) Calcd. 998.2090, Obsd. 998.211507 (32.52%); (M + H) Calcd. 976.2271, Obsd. 976.2342 (87.33%).

**Fulleropyrrolidine derivative (25)²₅, thirty** Fulleropyrrolidine derivative (22) (25 mg, 0.022 mmol) was dissolved in dichloromethane (5 mL). Under nitrogen, trifluoroacetic acid (5 mL) was added dropwise. The mixture was stirred at rt for 12 h. Then the solvent...
was removed under reduced pressure. After putting the resultant brown solid under vacuum for 8 h, the residue was retaken in dichloromethane (2 mL) under nitrogen. Then oxalyl chloride (2 mL) was added followed by DMF (1 drop). Gas was evolved vigorously. The mixture was stirred at rt for 12 h. Then the solvent was removed under reduced pressure and the resultant brown solid was put under vacuum for 8 h. The residue was retaken in dichloromethane (0.5 mL). Then under nitrogen, in another round-bottomed flask was placed di-tert-butyl 4-aminopyridine-2,6-dicarboxylate (16 mg, 0.054 mmol). Dichloromethane (0.5 mL) and pyridine (1 mL) were added. Then the solution made by acid chloride was added dropwise via a syringe to the amine solution. The mixture was stirred at rt for 12 h. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (toluene/EtOAc 9:1) to yield brown solid (16 mg, 61%).

4-Chloropyridine-2,6-dicarbonyl dichloride (45) To a round-bottomed flask was added chelidamic acid (3.03 g, 15 mmol) and PCl₅ (9.42 g, 45 mmol). Under nitrogen, the mixture was heated to 125 °C (oil bath temperature) for 18 h. After cooled to rt, a distillation head was added and POCl₃ was distilled off at about 105 °C. Then a new receiver flask was added and the remaining mixture was distilled under vacuum (4 mm Hg). The product came off at 108 °C first as liquid, but condensed to solid at the receiver flask. White solid was resulted (3.24 g, 90%).

Di-tert-butyl 4-chloropyridine-2,6-dicarboxylate (49) 4-Chloropyridine-2,6-dicarbonyl dichloride (45) (3.2 g, 13 mmol) was dissolved in dichloromethane (20 mL).
To another flask, tert-BuOH (5 mL), pyridine (20 mL) and DMAP (0.5 g) was dissolved in dichloromethane (50 mL). Then the acid chloride solution was added over 5 min. Then the mixture was stirred at rt for 12 h. Excess tert-BuOH and pyridine were removed under reduced pressure. The solid residue was dispersed in dichloromethane (40 mL) and washed with water (2 * 20 mL), dried over magnesium sulfate. After concentrating the solution, it was purified by flash chromatography (hexanes/EtOAc 85:15) to yield white solid (2.57 g, 61%).

**Di-tert-butyl 4-azidopyridine-2,6-dicarboxylate (50)**

Di-tert-butyl 4-chloropyridine-2,6-dicarboxylate (49) (4.3085 g, 3.5 mmol) was dissolved in DMF (42 mL). Then NaN₃ (8.9422 g, 35 mmol) was added. The mixture was stirred at 50 °C for 12 h. Then DMF was removed by Kugelrohr distillation at 60 °C. The residue was dissolved in dichloromethane (60 mL). The solution was washed by water (2 * 30 mL). The yellow organic phase was dried over magnesium sulfate. Flash chromatography by hexanes/EtOAc 10:1 resulted di-tert-butyl 4-azidopyridine-2,6-dicarboxylate (50) as white waxy solid (4.28 g, 97%).

**G0-N₃ (55)**

Di-tert-butyl 4-azidopyridine-2,6-dicarboxylate (50) (26 mg, 0.081 mmol) was dissolved in dichloromethane (1.5 mL). Under nitrogen, trifluoroacetic acid (1.5 mL) was added dropwise. The mixture was stirred at rt for 3 h. Then the solvent was removed under reduced pressure. After putting the resultant solid under vacuum for 8 h, the residue was retaken in dichloromethane (1.3 mL) under nitrogen. Then oxalyl chloride (1.3 mL) was added followed by DMF (1 drop). Gas was evolved vigorously. The
mixture was stirred at rt for 2 h. Then the solvent was removed under reduced pressure and the resultant solid was put under vacuum for 8 h. The residue was retaken in chloroform (0.8 mL). Then under nitrogen, in another round-bottomed flask was placed 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (107 mg, 0.17 mmol). Chloroform (0.7 mL) and pyridine (1.2 mL) were added. Then the solution of acid chloride was added dropwise via a syringe to the amine solution. The mixture was stirred at rt for 12 h. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (CH$_2$Cl$_2$/petroleum ether 75:25) to yield purple solid (76 mg, 65%). $^1$H-NMR (250 MHz, CDCl$_3$) $\delta$ -2.76 (s, 4H, pyrrole-NH), 7.74 (m, 18H, porphyrin-$_m$/p-phenyl), 8.11 (s, 2H, Ar-H), 8.22 (m, 20H, porphyrin-o-phenyl, porphyrin-amino-phenyl), 8.88 (m, 16H, pyrrole), 9.78 (s, 2H, NH); IR (CDCl$_3$, cm$^{-1}$) 3384, 3322 ($\nu_{\text{NH}}$), 3066 ($\nu_{\text{C-H}}$), 2124 ($\nu_{\text{N3}}$), 1688 ($\nu_{\text{C=O}}$); MS for C$_{95}$H$_{62}$N$_{14}$O$_2$ (MALDI-TOF) (M + H) Calcd. 1431.5258, Obsd. 1431.56; (M + K) Calcd. 1469.4817, Obsd. 1469.59.

$\text{G0-NH}_2$ (62)$^{33}$ G0-N$_3$ (55) (30 mg, 0.021 mmol) was dissolved in chloroform (1.5 mL). Under nitrogen, triethyl amine (0.5 mL) and propane-1,3-dithiol (0.3 mL) were added. The mixture was stirred at rt for 12 h. The solvent was removed under reduced pressure. Then the residue was purified by flash chromatography (toluene/EtOAc 9:1) to yield purple solid (22.4 mg, 76%). $^1$H-NMR (250 MHz, CDCl$_3$) $\delta$ -2.77 (s, 4H, pyrrole-NH), 7.73 (m, 18H, porphyrin-$_m$/p-phenyl), 7.85 (s, 2H, Ar-H), 8.20 (m, 20H, porphyrin-o-phenyl, porphyrin-amino-phenyl), 8.83 (m, 12H, pyrrole), 8.91 (d, $J = 4.8$ Hz, 4H, pyrrole), 10.05 (s, 2H, NH); MS for C$_{95}$H$_{64}$N$_{12}$O$_2$ (MALDI-TOF) (M) Calcd. 1404.5275, Obsd. 1404.73; (M + K) Calcd. 1443.4912, Obsd. 1443.72.
Tetraphenylporphyrin (42)\textsuperscript{34,35,36} A solution of benzaldehyde (10.16 mL, 0.10 mol) in propionic acid (200 mL) was heated to 130°C. Then under dark, a solution of pyrrole (6.94 mL, 0.10 mol) in propionic acid (20 mL) was added dropwise. The mixture was heated to reflux for 1 h. After cooled to room temperature, the solvent was removed under reduced pressure. The dark solid was retaken in chloroform and flash chromatography (chloroform) afforded purple tetraphenylporphyrin 42 (2.889 g, 19%).

\textsuperscript{1}H-NMR (250 MHz, CDCl\textsubscript{3}) \delta -2.74 (s, 2H, pyrrole NH), 7.76 (m, 12H, m/p phenyls), 8.23 (m, 8H, o-phenyl), 8.86 (s, 8H, pyrrole); \textsuperscript{13}C-NMR (62.9 MHz, CDCl\textsubscript{3}) \delta 120.2, 126.7, 127.7, 134.6, 142.2; UV-vis (\textlambda_{\text{max}} CH\textsubscript{2}Cl\textsubscript{2}) (log e) 416 (5.42), 514 (4.30), 550 (3.91), 592 (3.74), 646 (3.59); IR (CDCl\textsubscript{3}, cm\textsuperscript{-1}) 3322 (vNH\textsubscript{1}), 1598 (vC-C); HRMS for C\textsubscript{44}H\textsubscript{30}N\textsubscript{4} (ES) (M + Na) Calcd. 637.2363, Obsd. 637.2381 (17.24%); (M + H) Calcd. 615.2549, Obsd. 615.2596 (92.20%).

5-(4-Nitrophenyl)-10,15,20-triphenylporphyrin (43)\textsuperscript{37} Under nitrogen, to a solution of tetraphenylporphyrin (42) (1.7026 g, 2.8 mmol) in dichloromethane (250 mL) was added twice concentrated nitric acid (70%, d = 1.42, 4.02 mL, 64 mmol) through an addition funnel at 0–5°C. The mixture was stirred for another 3 h. Then the mixture was washed by water and sodium bicarbonate solution, and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure. Purple solid was resulted. TLC showed two spots with 42 at R\textsubscript{f} = 0.9 and 43 at R\textsubscript{f} = 0.8 by using chloroform.

5-(4-Aminophenyl)-10,15,20-triphenylporphyrin (52)\textsuperscript{38} The purple solid (mixture of 42 and 43) from nitration was dissolved in ethanol (100 mL) and concentrated
hydrochloric acid (80 mL). Under nitrogen, tin (II) chloride dihydrate (10.7776 g, 48 mmol) was added, and the solution was heated to 65°C for 1.5 h. Then the solution was cooled to room temperature. 200 mL water was added, and the mixture was adjusted to PH = 8 with concentrated ammonium hydroxide. The solution was extracted with 500 mL chloroform and the organic phase was washed by water and dried over magnesium sulfate. This solution was concentrated to 80 mL and flash chromatography (dichloromethane) afforded unreacted 42 and purple 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (52) (1.1 g, 63%). \(^1\)H-NMR (250 MHz, CDCl\(_3\)) \(\delta\) 2.72 (s, 2H, pyrrole NH), 3.96 (s, 2H, NH\(_2\)), 7.02 (d, 2H, \(J = 8.3\) Hz, aminophenyl), 7.75 (m, 9H, \(m/p\) phenyl), 7.99 (d, 2H, \(J = 8.3\) Hz, aminophenyl), 8.22 (m, 6H, o-phenyl), 8.84 (m, 6H, pyrrole), 8.94 (d, 2H, \(J = 4.75\) Hz, pyrrole); \(^13\)C-NMR (100 MHz, CDCl\(_3\)) \(\delta\) 113.5, 119.8, 120.1, 121.0, 126.7, 127.7, 132.4, 134.6, 135.7, 142.3, 142.4, 146.0; UV-vis (\(\lambda_{max}\) CH\(_2\)Cl\(_2\)) (log \(\varepsilon\)) 420 (5.43), 518 (4.16), 554 (3.91), 592 (3.63), 650 (3.57); IR (CDCl\(_3\), cm\(^{-1}\)) 3459, 3398 (\(\nu_{NH2}\)), 3323 (\(\nu_{NH}\), pyrrole), 1620 (\(\nu_{C=\cdot C-\cdot N}\)), 1515 (\(\nu_{NH2\ benz}\)); HRMS for C\(_{44}H\(_{31}\)N\(_5\) (ES) (M + Na) Calcd. 652.2472, Obsd. 652.2438 (19.77%); (M + H) Calcd. 630.2658, Obsd. 630.2712 (75.24%).

1,8:4,5-Naphthalenetetracarboxydiimide Derivative -- diallylic ester (90)\(^39\) A solution of diallyl 5-amino-2-methoxyisophthalate (403.6 mg, 1.4 mmol) and naphthalene-1,4,5,8-tetracarboxylic dianhydride (371.7 mg, 1.4 mmol) in pyridine (60 ml) was heated to reflux for 0.5 h. Then n-butylamine (123.4 \(\mu\)L, 1.2 mmol) was added dropwise. The mixture was refluxing for another 6.5 h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was retaken in dichloromethane and
purified by flash chromatography with dichloromethane/ethyl acetate (100:3) to give 90 (180 mg, 22%) as pink solid. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 0.99 (t, $J = 7.5$ Hz, 3H, 4-H(nBu)), 1.46 (m, 2H, 3-H(nBu)), 1.74 (m, 2H, 2-H(nBu)), 4.01 (s, 3H, -OCH$_3$), 4.21 (t, $J = 7.5$ Hz, 2H, 1-H(nBu)), 4.81 (dt, $J = 1.2$, 5.6 Hz, 4H, allyl-sp$^2$-CH$_2$), 5.27 (dq, $J = 1.2$, 2.4, 10.2 Hz, 2H, allyl-sp$^2$-CH$_2$), 5.40 (dq, $J = 1.2$, 2.4, 17.2 Hz, 2H, allyl-sp$^2$-CH$_2$), 6.00 (m, 2H, allyl-sp$^2$-CH), 7.96 (s, 2H, Ar-H), 8.79 (s, 4H, naphthalene-H); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 164.10, 162.81, 162.67, 160.59, 135.68, 131.67, 131.60, 131.05, 129.51, 127.75, 127.25, 126.85, 126.28, 119.15, 66.28, 64.06, 40.87, 30.16, 20.35, 13.81; UV-vis ($\lambda_{max}$ CH$_2$Cl$_2$) (log $\epsilon$) 238 (4.81), 360 (4.52), 382 (4.60); IR (CDCl$_3$, cm$^{-1}$) 3086, 2961, 2935, 2874 ($\nu_{CH}$), 1710 ($\nu_{ester C\equiv O}$), 1669 ($\nu_{imide C\equiv O}$), 1582 ($\nu_{C\equiv C}$), 1247 ($\nu_{as ester C\equiv O\equiv C}$), 984 ($\delta_{trans CH\equiv CH}$), 910 ($\omega_{CH_2}$); HRMS for C$_{33}$H$_{28}$N$_{5}$O$_9$ (ES) (M + Na) Calcd. 619.1687, Obsd. 619.1669 (100%).

1,8,4,5-Naphthenetetracarboxydümide Derivative – dicarboxylic acid (91)$^{19}$ To a flame-dried flask was added PPh$_3$ (66.02 mg, 0.25 mmol) and Pd$_2$(dba)$_3$·CHCl$_3$ (26.05 mg, 0.025 mmol) under nitrogen. Then dry THF (2.52 mL) was added. The solution was stirred at room temperature for 0.5 h until it became golden orange. To another flame-dried flask was added N,N-dimethylbarbituric acid (78.59 mg, 0.50 mmol) and 90 (150 mg, 0.25 mmol) under nitrogen. Then dry THF (5 mL) was added. The solution was stirred at room temperature until the entire solid dissolved. Then the catalyst solution containing Pd(0) (1.26 mL) was added via a syringe. The mixture was stirred for 3 h. Then solvent was removed under reduced pressure. The residue was retaken in dichloromethane. This suspension was filtered and resulted solid was washed several
times by dichloromethane to give 91 as pink solid (94.8 mg, 73%). $^1$H-NMR (400 MHz, DMSO) δ 0.94 (t, $J = 7.5$ Hz, 3H, 4-H(nBu)), 1.39 (m, 2H, 3-H(nBu)), 1.66 (m, 2H, 2-H(nBu)), 3.90 (s, 3H, -OCH$_3$), 4.08 (t, $J \approx 7.5$ Hz, 2H, 1-H(nBu)), 7.93 (s, 2H, Ar-H), 8.69 (q, $J = 7.6$, 12.4 Hz, 4H, naphthalene-H); $^{13}$C-NMR (100 MHz, DMSO) δ 13.70, 19.79, 29.55, 40.14, 63.08, 126.24, 126.48, 126.58, 126.89, 128.36, 130.33, 130.39, 134.16, 157.67, 162.65, 162.95, 166.33; HRMS for C$_{27}$H$_{30}$N$_2$O$_5$ (ES) (M + Na) Calcd. 539.1061. Obsd. 539.1083 (10.20%).

**G1-I-B (94)**\(^{19}\) To a suspension of 91 (40 mg, 0.078 mmol) in dichloromethane (2 mL) was added oxalyl chloride (54.1 µL, 0.62 mmol) and DMF (1 drop) under nitrogen. The mixture turned to homogeneous solution gradually. It was stirred at room temperature for 1.5 h. Then, the solution was removed under reduced pressure to give the diacid chloride as light pink solid, which was put under vacuum for 12 h. Then the resultant solid was redissolved in dichloromethane (0.8 mL). Under nitrogen, 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (52) (97.52 mg, 0.16 mmol) and DMAP (3.8 mg, 0.031 mmol) were dissolved in dichloromethane (1 mL) and pyridine (0.7 mL). This solution was cooled by an ice bath and then was added the diacid chloride solution dropwise. The whole mixture was stirred at room temperature for 12 h. The solvent was then removed and the residue was retaken in dichloromethane, and was purified by flash chromatography (dichloromethane: ethyl acetate = 40 : 1) to give G1-I-B (94) as purple solid (103 mg, 76%). $^1$H-NMR (250 MHz, CDCl$_3$) δ -3.07 (s, 4H, pyrrole NH), 0.92 (t, $J = 7.3$ Hz, 3H, 4-H(nBu)), 1.36 (m, 4H, 2-H(nBu), 3-H(nBu)), 3.88 (t, $J = 7.6$ Hz, 2H, 1-H(nBu)), 4.54 (s, 3H, OCH$_3$), 7.74 (m, 20H, porphyrin-<i>m</i>/<i>p</i>-phenyl, porphyrin-amiophenyl), 7.99 (d, $J =$
7.5 Hz, 2H, porphyrin-aminophenyl), 8.21 (m, 20H, porphyrin-o-phenyl, porphyrin-aminophenyl, naphthalene-H), 8.34 (s, 2H, Ar-H), 8.82 (s, 8H, pyrrole), 8.86 (d, $J = 4.9$ Hz, 4H, pyrrole), 8.95 (d, $J = 4.9$ Hz, 4H, pyrrole), 9.71 (s, 2H, amide NH); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 13.76, 20.26, 29.83, 40.34, 65.03, 118.77, 119.26, 120.28, 120.31, 123.11, 123.37, 123.82, 123.95, 126.80, 126.85, 127.82, 128.63, 129.98, 131.30, 131.94, 134.71, 135.62, 137.74, 138.64, 142.09, 155.77, 160.48, 161.66, 162.30; UV-vis ($\lambda_{max}$ CH$_2$Cl$_2$) (log $e$) 238 (4.91), 362 (4.87), 382 (4.92), 414 (5.45), 516 (4.61), 552 (4.30), 592 (4.08), 646 (3.96); IR (CDCl$_3$, cm$^{-1}$) 3321 (v$_{NH}$), 3061, 3029, 2962 (v$_{C-H}$), 1706, 1668 (v$_{C-O}$), 1584 (v$_{C-C}$); MS for C$_{115}$H$_{78}$N$_{12}$O$_7$ (MALDI-TOF) (M) calcd. 1738.6116, obsd. 1738.86; (M + Na) calcd. 1761.60, obsd. 1761.89; $^{1}$HRMS for C$_{115}$H$_{78}$N$_{12}$O$_7$ (ES) (M + Na) Calcd. 1762.6042, Obsd. 1762.6119 (52.04%).

**G1-I-B-Zn (97)**

A solution of G1-I-B (94) (22.8 mg, 0.013 mmol) in dichloromethane (2 mL) was added zinc acetate dihydrate (57.5 mg, 0.26 mmol) under nitrogen. This solution was refluxed for 4 h. Then after cooled, it was applied to column and was purified by flash chromatography (dichloromethane: ethyl acetate = 10:1) to give G1-I-B-Zn (97) as purple solid (15.23 mg, 62%). $^1$H-NMR (250 MHz, THF-D$_5$) $\delta$ 0.86 (t, $J = 7.3$ Hz, 3H, 4-H(nBu)), 1.40 (m, 4H, 2-H(nBu), 3-H(nBu)), 3.84 (t, 2H, 1-H(nBu)), 4.47 (s, 3H, OCH$_3$), 7.47 (d, $J = 7.8$ Hz, 2H, porphyrin-aminophenyl), 7.66 (m, 20H, porphyrin-m/p-phenyl, porphyrin-aminophenyl), 8.05 (s, 2H, Ar-H), 8.22 (m, 20H, porphyrin-o-phenyl, porphyrin-aminophenyl, naphthalene-H), 8.76 (s, 8H, pyrrole), 8.80 (d, $J = 4.6$ Hz, 4H, pyrrole), 8.95 (d, $J = 4.6$ Hz, 4H, pyrrole), 10.38 (s, 2H, amide NH); $^{13}$C-NMR (100 MHz, THF-D$_5$) $\delta$ 14.31, 21.25, 31.20, 41.10, 65.00, 108.57, 118.79,
121.67, 126.09, 127.33, 128.25, 129.75, 132.43, 134.51, 135.60, 136.13, 139.99, 144.67, 151.12, 162.31, 163.04, 164.50; UV-vis (λ_{max} THF) (log ε) 238 (4.71), 360 (4.56), 380 (4.52), 422 (5.33), 518 (3.80), 556 (4.51), 596 (4.12); IR (CDCl₃, cm⁻¹) 2960, 2928 (ν_C-H), 1709, 1668 (ν_C=O), 1597 (ν_C=C); MS for C₁₁₅H₇₅N₁₂O₇Zn₂ (MALDI-TOF) (M) calcd. 1862.4386, obsd. 1862.90; (M + Na) calcd. 1885.4284, obsd. 1885.98.

1,8:4,5-Naphthalenetetracarboxydiimide Derivative (80)³⁹ A mixture of naphthalene-1,4,5,8-tetracarboxylic dianhydride (250 mg, 0.93 mmol) and aniline (106.2 μL, 1.2 mmol) in pyridine (40 mL) was heated to reflux for 2 h under nitrogen. After cooled to room temperature, butylamine (76.8 μL, 0.78 mmol) was added. The mixture was refluxed for another 2.5 h. Then the solvent was removed under reduced pressure and the residue was retaken in dichloromethane, and was purified by flash chromatography (dichloromethane: ethyl acetate = 200 : 5) to give 80 as pink solid (65.31 mg, 21%).²¹ ¹H-NMR (250 MHz, CDCl₃) δ 0.99 (t, J = 7.2 Hz, 3H, 4-H(nBu)), 1.46 (m, 2H, 3-H(nBu)), 1.74 (m, 2H, 2-H(nBu)), 4.21 (t, J = 7.5 Hz, 2H, 1-H(nBu)), 7.31 (m, 2H, Ar-H), 7.54 (m, 3H, Ar-H), 8.78 (s, 4H, naphthalene-H);¹³C-NMR (100 MHz, CDCl₃) δ 13.83, 20.35, 30.16, 40.82, 126.70, 126.81, 126.93, 127.05, 128.46, 129.20, 129.58, 131.01, 131.34, 134.60, 162.76, 163.00; UV-vis (λ_{max} CH₂Cl₂) (log ε) 240 (4.70), 360 (4.53), 382 (4.60); IR (CDCl₃, cm⁻¹) 2963, 2934 (ν_C-H), 1708, 1669 (ν_C=O), 1581 (ν_C=C); HRMS for C₂₄H₁₈N₂O₄ (ES) (M + Na) Calcd. 421.1159, Obsd. 421.1165 (32.68%).

G0-I-B-NO₂ (78)¹⁹ To a suspension of 2-methoxy-5-nitroisophthalic acid (20 mg, 0.083 mmol) in dichloromethane (1.5 mL) was added oxalyl chloride (58 μL, 0.66 mmol) and
DMF (1 drop) under nitrogen. The mixture turned to homogeneous solution gradually. It was stirred at room temperature for 3 h. Then, the solution was removed under reduced pressure and was put under vacuum for 12 h. Then the resultant solid was redissolved in dichloromethane (1.5 mL). Under nitrogen, 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (52) (104.4 mg, 0.17 mmol) and DMAP (4.1 mg, 0.034 mmol) were dissolved in dichloromethane (1 mL) and pyridine (1 mL). This solution was cooled by an ice bath and then was added the diacid chloride solution dropwise. The whole mixture was stirred at room temperature for 12 h. The solvent was then removed and the residue was re taken in dichloromethane, and was purified by flash chromatography by dichloromethane to give G0-I-B-NO2 (78) as purple solid (100 mg, 82%). $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ -2.76 (s, 4H, pyrrole-NH), 4.45 (s, 3H, OCH$_3$), 7.73 (m, 18H, porphyrin-m/p-phenyl), 8.11 (d, $J$ = 8.4 Hz, 4H, porphyrin-aminophenyl), 8.20 (m, 12H, porphyrin-o-phenyl), 8.29 (d, $J$ = 8.4 Hz, 4H, porphyrin-aminophenyl), 8.85 (m, 12H, pyrrole), 8.90 (d, $J$ = 4.8 Hz, 4H, pyrrole), 9.14 (s, 2H, Ar-H), 9.41 (s, 2H, NH); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 64.84, 118.57, 118.97, 120.29, 120.37, 126.71, 127.76, 128.81, 129.69, 129.96, 131.19, 134.55, 134.57, 135.44, 137.02, 139.43, 142.11, 144.53, 159.59, 161.12; UV-vis ($\lambda_{\text{max}}$ CD$_2$Cl$_2$) (log e) 414 (5.45), 516 (4.62), 552 (4.39), 590 (4.31), 646 (4.06), 678 (3.74); IR (CDCl$_3$, cm$^{-1}$) 3378, 3322 ($\nu_{\text{NH}}$), 3056, 2985 ($\nu_{\text{CH}}$), 1730, 1683 ($\nu_{\text{C=O}}$), 1594 ($\nu_{\text{C=C}}$), 1522, 1350 ($\nu_{\text{NO2}}$); MS for C$_{97}$H$_{65}$N$_{11}$O$_{5}$ (MALDI-TOF) (M) calcd. 1463.5170, obsd. 1463.65; HRMS for C$_{97}$H$_{65}$N$_{11}$O$_{5}$ (ES) (M + Na) Calcd. 1487.5096, Obsd. 1487.5206 (92.81%); (M + H) Calcd. 1465.5276, Obsd. 1465.5340 (45.33%).
G0-I-B-NH₂ (81)³⁸ G0-I-B-NO₂ (78) (25 mg, 0.017 mmol) was dissolved in THF (6 mL). Under nitrogen, tin (II) chloride dihydrate (240 mg, 1.1 mmol) was added. At this moment, the mixture turned green. It was stirred at room temperature for 12 h. Then, water (20 mL) was added to the reaction mixture. The PH value of the solution was adjusted to 8 by adding aqueous ammonia hydroxide. The mixture was extracted with dichloromethane. The organic layer was washed by water and dried over anhydrous magnesium sulfate. It was purified by flash chromatography (dichloromethane : ethyl acetate = 100 : 15) to give G0-I-B-NH₂ (81) as purple solid (15.17 mg, 62%). ¹H-NMR (400 MHz, CDCl₃) δ 2.72 (s, 4H, pyrrole-NH), 4.32 (s, 3H, OCH₃), 7.74 (m, 20H, porphyrin-m/p-phenyl, Ar-H), 8.20 (m, 16H, porphyrin-aminophenyl, porphyrin-o-phenyl), 8.30 (d, J = 8.4 Hz, 4H, porphyrin-aminophenyl), 8.85 (m, 12H, pyrrole), 8.95 (d, J = 4.8 Hz, 4H, pyrrole), 9.85 (s, 2H, NH); ¹³C-NMR (100 MHz, CDCl₃) δ 64.74, 118.49, 119.37, 120.22, 120.78, 126.35, 126.68, 127.72, 128.69, 131.22, 134.25, 134.54, 135.36, 137.78, 138.64, 141.83, 142.13, 144.30, 147.57, 163.14; UV-vis (λₘₐₓ CH₂Cl₂) (log ε) 414 (5.40), 516 (4.46), 552 (4.16), 592 (3.94), 648 (3.82); IR (CDCl₃, cm⁻¹) 3322 (νN-H), 3060, 3028 (νC=H), 1711, 1674 (νC=O), 1593 (νC=C); MS for C₉₇H₆₇N₁₁O₃ (MALDI-TOF) (M) calcd. 1433.5428, obsd. 1433.75; HRMS for C₉₇H₆₇N₁₁O₃ (ES) (M + Na) Calcd. 1457.5354, Obsd. 1457.5306 (72.01%).

5-(4-(2-Nitrophenylcarbamoyl)phenyl)-10,15,20-triphenylporphyrin (98)¹⁹ To a suspension of 2-nitrobenzoic acid (42 mg, 95%, 0.24 mmol) in dichloromethane (2 mL) was added oxalyl chloride (87.70 μL, 1.0 mmol) and DMF (1 drop) under nitrogen. The mixture turned to homogeneous solution gradually. It was stirred at room temperature for
1.5 h. Then, the solution was removed under reduced pressure and was put under vacuum for 12 h. Then the resultant solid was redissolved in dichloromethane (1.5 mL). Under nitrogen, 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (52) (150.2 mg, 0.24 mmol) and DMAP (5.83 mg, 0.048 mmol) were dissolved in dichloromethane (1 mL) and pyridine (1.2 mL). This solution was cooled by an ice bath and then was added the 2-nitrobenzoyl chloride solution dropwise. The whole mixture was stirred at room temperature for 12 h. The solvent was then removed and the residue was retaken in dichloromethane, and was purified by flash chromatography (dichloromethane : ethyl acetate = 400 : 16) to give 98 as purple solid (161.4 mg, 87%). $^1$H-NMR (400 MHz, CDCl$_3$) δ -2.74 (s, 2H, pyrrole-NH), 7.50 (t, $J = 7.4$ Hz, 1H, Ar-H), 7.62 (d, $J = 8.0$ Hz, 1H, Ar-H), 7.67 (t, $J = 7.4$ Hz, 1H, Ar-H), 7.74 (m, 9H, porphyrin-$m/p$-phenyl), 7.86 (d, $J = 8.0$ Hz, 2H, porphyrin-aminophenyl), 8.06 (d, $J = 8.0$ Hz, 1H, Ar-H), 8.16 (d, $J = 8.0$ Hz, 2H, porphyrin-aminophenyl), 8.21 (m, 6H, porphyrin-o-phenyl), 8.86 (m, 8H, pyrrole); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 118.60, 119.29, 120.29, 124.76, 126.74, 127.78, 128.63, 130.84, 132.84, 133.99, 134.58, 134.61, 135.19, 137.08, 138.98, 142.13, 142.15, 146.28, 164.73; UV-vis ($\lambda_{\text{max}}$ CH$_2$Cl$_2$) (log ε) 414 (5.43), 516 (4.42), 552 (4.10), 592 (3.91), 646 (3.80); IR (CDCl$_3$, cm$^{-1}$) 3418, 3322 ($\nu_{\text{N-H}}$), 3061, 3029 ($\nu_{\text{C-H}}$), 1689 ($\nu_{\text{C=O}}$), 1589 ($\nu_{\text{C=C}}$), 1533, 1350 ($\nu_{\text{NO2}}$); HRMS for C$_{51}$H$_{33}$N$_6$O$_3$ (ES) (M + Na) Calcd. 801.2584, Obsd. 801.2558 (87.80%); (M + H) Calcd. 779.2771, Obsd. 779.2823 (100%).

5-(4-(2-Aminophenylcarbamoyl)phenyl)-10,15,20-triphenylporphyrin (99)$^{38}$ 5-(4-(2-Nitrophenylcarbamoyl)phenyl)-10,15,20-triphenylporphyrin (98) (100 mg, 0.13 mmol) was dissolved in THF (25 mL). Under nitrogen, tin (II) chloride dihydrate (580 mg, 2.6
mmol) was added. The mixture was stirred at room temperature for 12 h. Then, sodium bicarbonate solution was added to the reaction mixture until the mixture turned from green to red. The mixture was extracted with chloroform. The organic layer was washed by water and dried over anhydrous magnesium sulfate. It was purified by flash chromatography (dichloromethane : ethyl acetate = 20 : 1) to give 99 as purple solid (56 mg, 58%). $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ -2.67 (s, 2H, pyrrole-NH), 5.60 (s, 2H, NH$_2$), 6.74 (d, $J$ = 8.0 Hz, 1H, Ar-H), 6.78 (t, $J$ = 8.0 Hz, 1H, Ar-H), 7.30 (t, $J$ = 8.0 Hz, 1H, Ar-H), 7.56 (d, $J$ = 8.0 Hz, 1H, Ar-H). 7.78 (m, 9H, porphyrin-$m$/$p$-phenyl), 7.96 (d, $J$ = 8.4 Hz, 2H, porphyrin-aminophenyl), 8.25 (m, 8H, porphyrin-$o$-phenyl, porphyrin-aminophenyl), 8.91 (m, 6H, pyrrole), 8.96 (d, $J$ = 4.8 Hz, 2H, pyrrole); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 116.18, 117.00, 117.72, 118.67, 119.60, 120.25, 120.27, 126.76, 127.34, 127.78, 131.13, 133.00, 134.62, 135.24, 137.74, 138.29, 142.22, 149.19, 167.90; UV-vis ($\lambda_{\text{max}}$ CH$_2$Cl$_2$) (log $\varepsilon$) 416 (5.45), 516 (4.35), 552 (4.06), 592 (3.86), 648 (3.75); IR (CDCl$_3$, cm$^{-1}$) 3500, 3435, 3370, 3322 ($v_{\text{N-H}}$), 3060, 3029 ($v_{\text{C-H}}$), 1663 ($v_{\text{C=O}}$), 1586 ($v_{\text{C=C}}$); HRMS for C$_{51}$H$_{36}$N$_4$O (ES) (M + Na) Calcd. 771.2843, Obsd. 771.2838 (89.55%); (M + H) Calcd. 749.3029, Obsd. 749.3133 (100%).

**G1-II-B (100)** To a suspension of 91 (20.70 mg, 0.040 mmol) in dichloromethane (1 mL) was added oxalyl chloride (28 µL, 0.32 mmol) and DMF (1 drop) under nitrogen. The mixture turned to homogeneous solution gradually. It was stirred at room temperature for 3 h. Then, the solution was removed under reduced pressure to give the diacid chloride as light pink solid, which was put under vacuum for 12 h. Then the resultant solid was redissolved in dichloromethane (0.5 mL). Under nitrogen, 99 (60 mg,
0.080 mmol) and DMAE (2 mg, 0.016 mmol) were dissolved in dichloromethane (0.5 mL) and pyridine (0.5 mL). This solution was cooled by an ice bath and then was added the diacid chloride solution dropwise. The whole mixture was stirred at room temperature for 12 h. The solvent was then removed and the residue was retaken in dichloromethane, and was purified by flash chromatography (dichloromethane: ethyl acetate = 16 : 1) to give G1-II-B (100) as purple solid (36.3 mg, 46%). $^1$H-NMR (400 MHz, THF-d$_8$) $\delta$ 0.74 (t, $J = 7.2$ Hz, 3H, 4-H(nBu)), 1.05 (m, 2H, 3-H(nBu)), 1.14 (m, 2H, 2-H(nBu)), 2.93 (t, $J = 6.8$ Hz, 2H, 1-H(nBu)), 4.42 (s, 3H, OCH$_3$), 7.02 (t, $J = 7.6$ Hz, 2H, Ar-H), 7.39 (t, $J = 7.6$ Hz, 2H, Ar-H), 7.65 (m, 12H, porphyrin-m/p-phenyl), 7.75 (m, 10H, porphyrin-m/p-phenyl, Ar-H), 8.07 (d, $J = 8.4$ Hz, 4H, porphyrin-aminophenyl), 8.14 (s, 2H, Ar-H), 8.19 (m, 20H, porphyrin-o-phenyl, porphyrin-aminophenyl, naphthalene-H), 8.80 (m, 16H, pyrrole), 10.01 (s, 2H, amide NH), 11.76 (s, 2H, amide NH); $^{13}$C-NMR (400 MHz, THF-d$_8$) $\delta$ 14.05, 20.93, 30.53, 40.30, 64.76, 119.47, 120.91, 121.05, 124.06, 126.52, 127.60, 127.65, 128.60, 129.93, 130.49, 130.83, 132.18, 132.37, 135.44, 135.88, 136.06, 138.53, 139.57, 140.23, 143.36, 157.72, 161.96, 163.34, 163.92, 168.27; UV-vis ($\lambda_{max}$ THF) (log $e$) 238 (4.99), 362 (4.88), 380 (4.93), 412 (5.44), 516 (4.62), 550 (4.34), 594 (4.09), 650 (3.97); IR (THF, cm$^{-1}$) 3571, 3505, 3317 ($\nu_{NH}$), 3102, 3057 ($\nu_{C-H}$), 1707, 1670 ($\nu_{C=O}$), 1596 ($\nu_{C=C}$); MS for C$_{125}$H$_{88}$N$_{14}$O$_9$ (MALDI-TOF) (M + H) calcd. 1977.6937, obsd. 1977.95; (M + Na) calcd. 1999.6756, obsd. 1999.95; (M + K) calcd. 2015.6496, obsd. 2015.88; HRMS for C$_{129}$H$_{88}$N$_{14}$O$_9$ (ES) (M + Na) Calcd. 2000.6784, Obsd. 2000.6783 (100%).
LIST OF REFERENCES


42. From results of studies by Dr. David Modarelli at the University of Akron.

43. Chris Gabriel’s paper, to be submitted.

SpinWorks 2.0:

file: D:\Wy Files\research\NMR for MS\WYQ42\fid ext: <zg30>
transmitter freq: 250.131545 MHz
time domain size: 16384 points
width: 5175.98 Hz = 20.693046 ppm = 0.315917 Hz/pt
number of scans: 16

freq. of 0 ppm: 250.130012 MHz
processed size: 32768 complex points
LB: 0.300 Ga: 0.0000
Hz/cm: 144.778 ppm/cm: 0.57881

WYQ42
SpinWorks 2.0: test spectrum

WYQ55

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number of scans: 16
SpinWorks 2.0:

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number of scans: 74

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SpinWorks 2.0:

WYQ91

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time domain size: 32768 points
width: 8278.15 Hz = 20.868513 ppm = 0.252629 Hz/pt
number of scans: 128

freq. of 0 ppm: 400.130006 MHz
processed size: 16384 complex points
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SpinWorks 2.0:

WYQ94

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transform domain size: 16384 points
width: 5175.99 Hz = 20.893046 ppm = 0.315917 Hz/pt
number of scans: 16

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processed size: 32768 complex points
LB: 0.300 GB: 0.0000
Hz/cm: 144.778 ppm/cm: 0.57851
SpinWorks 2.0:

WYQ98

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transmitter freq: 400.132471 MHz
time domain size: 32768 points
width: 8278.15 Hz = 20.696513 ppm = 0.252629 Hz/pt
number of scans: 16

freq. of 0 ppm: 400.130017 MHz
processed size: 16384 complex points
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Hz/cm: 203.509  ppm/cm: 0.50861
SpinWorks 2.0:

WYQ42

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freq. of 0 ppm: 62.895239 MHz
processed size: 32768 complex points
LB: 1.000  GB: 0.0000
Hz/cm: 451.762  ppm/cm: 7.18205

PPM  150  140  130  120  110  100  90  80  70  60  50  40  30  20  10  0 -10

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number of scans: 381