J. Am. Chem. Soc. 1992, 114, 6227–6238

Electron Transfer in Bis-Porphyrin Donor–Acceptor Compounds with Polyphenylene Spacers Shows a Weak Distance Dependence

Anna Helms, David Heiler, and George McLendon*

Contribution from the Department of Chemistry, University of Rochester, Rochester, New York 14627. *Received March 1, 1991. Revised Manuscript Received April 3, 1992*

Abstract: A series of phenylene-bridged bis-porphyrin adducts have been synthesized, containing one, two, or three phenyl bridges. Complete synthetic details are provided. For studies of photochemical electron transfer, mixed metals were incorporated, with zinc in one porphyrin macrocycle and Fe^{III} (bis-imidazole) in the other macrocycle. When photoexcited, an electron is transferred from Zn to Fe^{III}. The rate of this process drops only slowly with distance: $k \alpha \exp(\beta r)$, with $\beta = 0.4$ Å^{-1}. This dependence can be predicted by a simple theory which assumes that the drop does *not* reflect increased distance, but rather reflects the break in conjugation which occurs at each phenyl juncture due to the biphenyl twist angle of ca. 50°. Inefficient overlap in this angle results in a rate drop of ca. 6-fold per phenyl ring, in good agreement with the observed results.

Introduction

Over the past few years, a number of groups have begun to examine the role of the intervening matrix in determining the electronic coupling between the electron donor and electron acceptor which makes possible electron-transfer reactions.[1-5] It has been found that, when the donor and acceptor are connected covalently via a rigid spacer, electron-transfer rates appear to be enhanced via through-bond couplings. In the present context, a particularly interesting set of experiments were reported by Heitele and Michel-Beyerle.[6] In their experiments, they observed that when aromatic spacers were employed, the distance dependence of the rate constant decreased significantly from that observed with aliphatic spacers. They found that for an increase of 4 Å the rate decreased by a factor of 20 with aromatic spacers as opposed to a factor of 100 decrease for a corresponding 4-Å spacing by aliphatic groups. They attribute this large difference to the occurrence of electron transfer via superexchange[6,7] for the aromatic spacers. To support this conclusion, experiments were conducted at a fixed distance while the energy levels of the aromatic spacers were varied. The electron-transfer rate constant was found to depend on the electronic structure of the spacer. This dependence, coupled with the weak distance dependence, indicates that the donor–acceptor interaction responsible for electron transfer is mediated by the spacer. In like manner, Sessler and co-workers have proposed a superexchange mechanism to explain the nonthermally activated electron-transfer reaction of a quinone-substituted, phenyl-linked, "gable" type porphyrin dimer.[5] Finally, using a series of bis-porphyrin compounds similar to those first reported by us, Maruyama et al. have reported a beautiful series of compounds in which the porphyrin to porphyrin electron-transfer rate seems to vary weakly with distance.[12]

Table I. Observed Fluorescence Decay Rate Constants for ZnP–FeP Dimers

spacer	distance (Å) (edge to edge)	$k_{et}(s^{-1})$
C_6H_4	5.8	$(4 \pm 1) \times 10^{10}$
$(C_6H_4)_2$	10.1	$(7 \pm 1) \times 10^9$
$(C_6H_4)_3$	14.4	$(1.1 \pm 1) \times 10^9$

We now report results for electron transfer in a systematic series of bis-porphyrin compounds which are rigidly connected by one, two, and three polyphenylene linkers (Figure 1). In all of the dimers, the spacing groups are based on rigid phenyl units which are structurally and chemically very similar. This series allows for measurements to be made over an edge to edge separation ranging from 5.8 to 14.1 Å. The results are well described by a simple theory which assumes delocalization *within* a phenyl ring, so that the rate is determined ultimately by the loss of conjugation at the ring junctures.

Results and Discussion

Using the synthetic procedures already outlined, we were able to prepare (Zn)porphyrin (phenylene)$_n$ porphyrin Fe^{III} (imidazole)$_2$ systems with $n = 1, 2, 3$ (Figure 1). The compound with $n = 1$ had been previously reported in a preliminary communication.[8] These results were also repeated as part of the elegant study by Maruyama.[12] No synthetic details were previously provided in either case. We found the $n = 3$ compound to be significantly less stable with respect to acid-catalyzed decomposition. The compound with $n = 4$ was also synthesized, but it readily decomposed on attempted TLC purification on alumina.

It had previously been shown that the absorption spectra of the linear mixed metal dimers could be adequately described in terms of a superposition of the absorption spectra of the two monomers.[8] From the lack of significant broadening of the B-bands, it can be determined that exciton coupling is small in the dimers. This is in contrast to the absorption spectra of cofacial dimers which exhibit band shifting and broadening indicative of electronic interaction between the subunits. It is well known that iron por-

---

(1) A general review of recent work can be found in the following monograph: *Electron Transfer in Organic, Inorganic and Biological Systems*; ACS Advances in Chemistry Series 228; American Chemical Society: Washington, D.C., 1991.

(2) Closs, G.; Calcaterra, L.; Green, N.; Penfield, K.; Miller, J. R. *J. Phys. Chem.* **1986**, *90*, 3073.

(3) Warman, J.; Haas, M.; Paddon Rowe, M.; Constanis, E.; Hush, N.; Verhoeven, J. *Nature* **1986**, *320*, 615.

(4) Wasielewski, M.; Niemcyzk, M. In *Porphyrins*; ACS Symposium Series 325; Gouterman, M., Rentzepis, P., Straub, K., Eds.; American Chemical Society: Washington, D.C., 1986.

(5) Sessler, J.; Johnson, M.; Liu, T.; Creager, S. *J. Am. Chem. Soc.* **1988**, *110*, 3659.

(6) Finckh, P.; Heitele, H.; Beyerle, M. M. *J. Phys. Chem.* **1988**, *92*, 6584 and references therein.

(7) Miller, J. R.; Beitz, J. *J. Chem. Phys.* **1981**, *74*, 6746.

(8) (a) Heiler, D.; McLendon, G.; Rogalskyj, P. *J. Am. Chem. Soc.* **1987**, *109*, 604. (b) Helms, A.; Heiler, D.; McLendon, G. *J. Am. Chem. Soc.* **1991**, *113*, 4325.

(9) Helms, A. Ph.D. Thesis, University of Rochester, Rochester, NY. The general synthetic scheme is outlined in the following: McLendon, G. *Acc. Chem. Res.* **1988**, *21*, 160.

(10) (a) Chang, C. K. *J. Heterocycl. Chem.* **1977**, *14*, 1285. (b) Chang, C. K.; Abdalmuhdi, I. *J. Org. Chem.* **1985**, *50*, 44. (c) Olah, G.; Tolgyesi, I. In *Friedel-Crafts and Related Reactions*; John Wiley and Sons: New York, 1964; Vol. 2, p 659.

(11) Bashkin, J.; McLendon, G.; Mukamel, S.; Marohn, J. *J. Phys. Chem.* **1990**, *94*, 4757.

(12) An increase in absorbance of ca. 750 nm, corresponding to the porphyrin cation radical, was observed for this series. The current results have been previously reported for the meso phenyl spacer in ref 8 and also by Osuka, A.; Maruyama, H.; Mataga, N.; Asaki, T.; Yamazaki, I.; Tamdi, H. *J. Am. Chem. Soc.* **1990**, *12*, 4958.

0002-7863/92/1514-6227$03.00/0

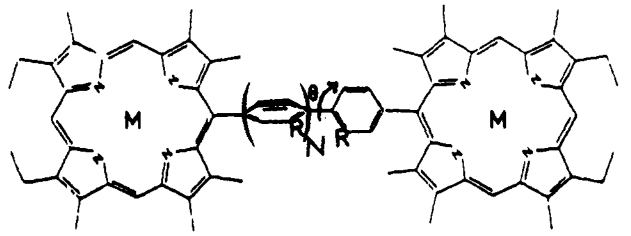


Figure 1. Schematic structures of the polyphenylene-bridged bisporphyrin adducts: M = Fe^{n}, Zn, n = 0, 1, 2. For the compounds reported here, R = H, CH, or $(CH_2)_2{}^{n}(CH_2)_3$.

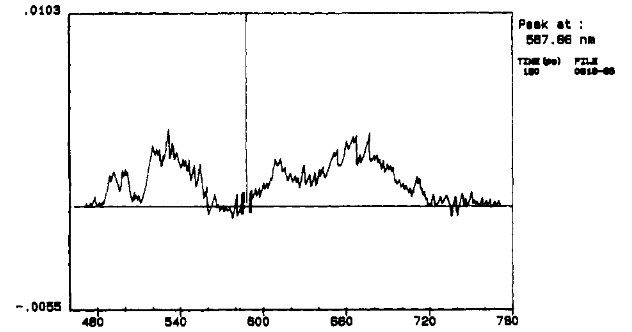


Figure 2. Pulse probe transient absorbance studies of compound **1** at a delay time of 10 ps after the pulse. Note the broad feature centered around 500 nm [assigned to Fe^{II}] and the cation radical feature above 600 nm. Analogous transient absorbance spectra of **1** and **2**, in the absence of imidazole, were already presented in ref 12.

phyrins have very short-lived excited electronic states, and thus do not emit. This is due to the mixing of different excited states, which produces strong vibronic couplings between the states. The result is rapid, radiationless decay of the initial excited state. The existence of low-energy d–d transitions also contribute to rapid excited-state deactivation. Therefore, the fluorescence spectra obtained for the dimers correspond to the zinc subunit alone. The lifetimes and associated quantum yields for the mixed metal dimers are greatly reduced from those of the dizinc dimers. This decrease can be attributed to electron transfer from the first excited singlet state of the zinc porphyrin [^{1}(ZnP)*] to the iron porphyrin. This lifetime decrease reflects electron transfer as the dominant decay pathway. This is demonstrated by the transient absorbance spectra, which show a decrease of the $S_1 \rightarrow S_n$ absorbance feature at ca. 450 nm, with concomitant growth of a broad feature at 480–520 nm and an associated broad feature between 600 and 700 nm which has been assigned to the ZnP^+ cation radical (Figure 2).

Similar spectra were obtained for all three dimers (n = 1, 2, 3). In the present studies, charge recombination occurred very quickly. This is consistent with the suggestion that the slow recombination rate previously reported for compound **1** by Maruyama in fact reflects rate-limiting ligand (re)addition. For the bis-imidazole adducts studied here, no change in coordination number accompanies Fe^{III} reduction, so that no such slow step is expected. Given the significant temporal overlap between the charge separation and recombination reactions, more accurate measurements of the transfer were obtained by picosecond single photon counting luminescence decay studies (Figure 3). The results of these studies are summarized in Table I. It is noteworthy that, for *highly* purified samples, quite similar rate estimates were obtained from simple steady-state luminescence spectra (Figure 4). Thus, these independent photophysical measurements give equivalent rate estimates, thereby increasing the reliability of such rate constants.

A plot of the natural log of these lifetimes vs the edge to edge separation distance is shown in Figure 5. From this plot, a phenomenological distance dependence can be obtained as

$$k = A_0 \exp(-\beta r)$$

The rate constants yield a value of β = 0.4 Å^{-1} for these compounds. Measured values of β for electron-transfer reactions of

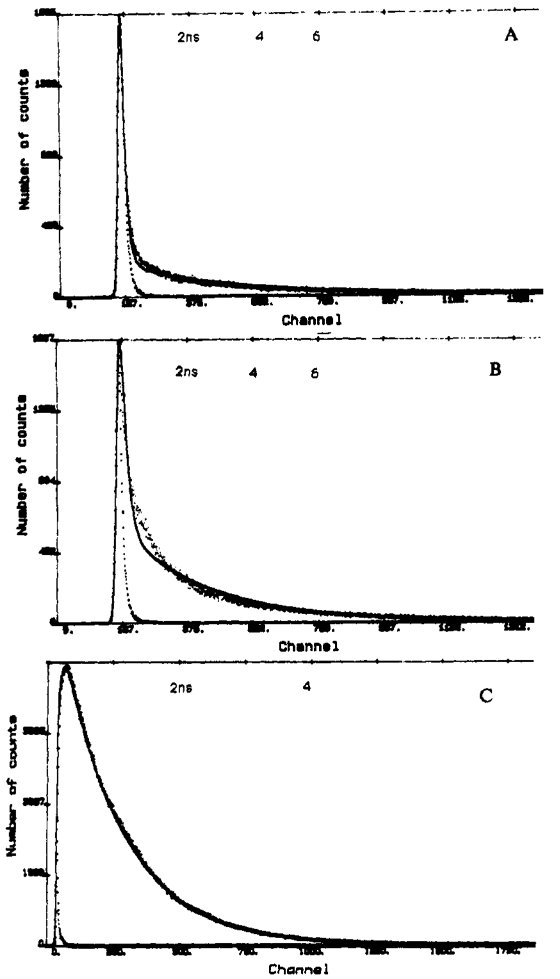


Figure 3. Single photon counting decay curves for compounds **1** (A), **2** (B), and **3** (C). The solid lines are fits of the data to lifetimes of (A) 25 ps and 3.0 ns, (B) 150 ps and 3.1 ns, and (C) 900 ps. Associated errors (from fits on independent samples) are given in Table I. Note, in the sample used in Figure 3B, the presence of a small amount of a slowly decaying impurity, which is due to residual zinc dimer in which Fe has not been incorporated.

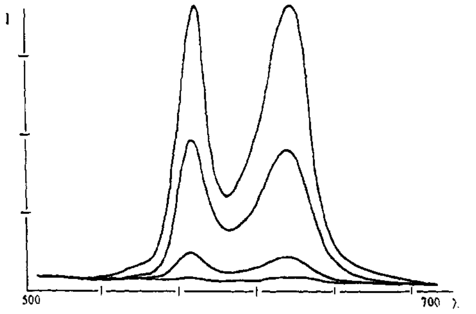


Figure 4. Steady-state luminescence studies of highly purified samples of compounds **1**–**3** and the "zinc only" dimers. The ratio of luminescence intensities closely matches that predicted from the photon counting results shown in Figure 3. Thus, when the samples are rigorously purified, simple emission spectra provide excellent estimates of the electron-transfer rate constants.

donor–acceptor pairs separated by aliphatic spacers typically yield values for α greater than 1 Å^{-1}.

However, it is not clear that "distance", per se, is the most appropriate parameter for describing electronic coupling when coupling proceeds by a superexchange (through-bond) pathway. One theoretical model, by Onuchic and Beratan, has explicitly treated the effect of bridging biphenyl spacers.[13] The *basic*

---

[13] Onuchic, J. N.; Beratan, D. N. *J. Am. Chem. Soc.* **1987**, *109*, 6771.

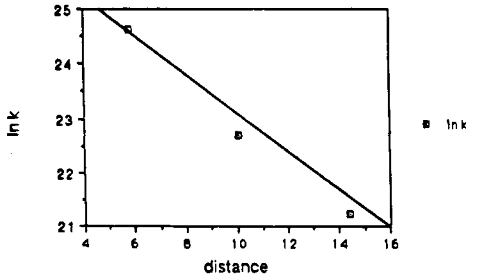


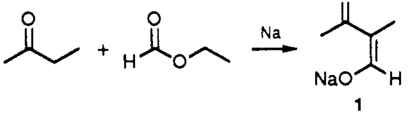
Figure 5. Plot of the rate of electron transfer (data from Figure 3) versus edge to edge distance in the bis-porphyrin series. The slope, $\beta = 0.4$ Å^{-1}.

assumption is that the exchange integral within the aromatic ring (β) is much larger than that between rings (γ), since conjugation between the rings is broken at the ring juncture due to nonbonded interactions[8b] which force (bi)phenyl into a nonplanar geometry. In this model, the ratio ($\nu = \gamma/\beta$) determines the overall coupling in the molecule. Quantitative predictions were difficult because of the dependence of coupling on angle.[8b,14] Using a simple assumption, they could predict that the rate would change by less than a factor of 10 per ring, in agreement with the present results. By using an empirical value of the angle dependence, obtained from previous studies of the angle dependence of electron transfer,[8b] we can better test this model. We take the angle θ between rings as $\theta \approx 50°$ ($\pm 5°$) from the known geometry of biphenyl. Using previous work from our lab[8b] on the angle dependence of electron-transfer rates in such compounds, we can set an empirical value for the ratio, ν: (roughly) a 7-fold drop in rate (at equivalent distance) occurs when the angle is varied from 0° to 50°. We thus predict a decay, per ring, of ca. 7-fold per ring, which is in excellent agreement with the observed data. By contrast, when $\theta = 0°$, there is *no* drop in rate in increasing the spacer length from one to two phenyl rings. This is the obvious prediction of the present model. This supports the assumption of the Onuchic–Beratan model and permits quantitation of that model. This was not possible for the original authors because, in their words, "a consistent set of experiments does not exist ... [to] normalize ϵ" (the tunneling matrix element). With the present publication, this problem is now overcome.

Experimental Section

Materials. All chemicals were purchased from either Aldrich, Fluka, or Siga. Solvents were used without further purification unless otherwise noted (in these cases, standard purification techniques were used[42]). High-resolution mass spectral determinations were performed by the Midwest Center for Mass Spectroscopy, a National Science Foundation Regional Instrument Facility (Grant No. CHE8211164). ^{1}H NMR spectra were obtained on a QE-300 GE NMR instrument. An HP 5890 series GC with tandem 5970 MSD was used for routine structural confirmation and as a purity check. All compounds reported here gave a *single* GC peak, with a mass spectrum corresponding to that of the parent ion. Static fluorescence measurements were made on a PE MPF-44A fluorescence spectrometer, and a PE Lambda Array 3840 UV/vis spectrophotometer was used to obtain absorption spectra.

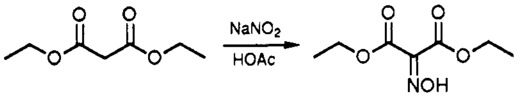
Synthesis. Compounds **1**–**10**[10a,b] and **16**[10c] have been previously reported, albeit with slightly altered routes. For completeness, the procedure used in our laboratories is presented here.



1

(1)

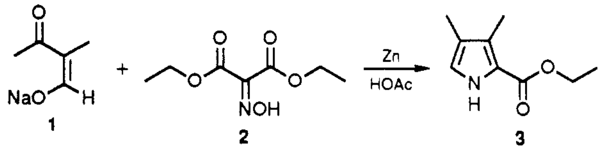
2-Methyl-3-oxo-1-butene 1-Oxide Sodium Salt (1). Ethyl acetoacetate (40.3 mL) and 45 mL of 2-butanone were placed in a 1-L round-bottom flask along with 500 mL of dry Et$_2$O and cooled to 0 °C in an ice/salt bath. A total of 11.5 g of Na was then added over 2 h maintaining the temperature at 0 °C. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The solids were filtered, washed with Et$_2$O, and dried to yield 55.67 g (91%) of **1**: ^{1}H NMR (CDCl$_3$) δ 8.96 (s, 1 H), 2.10 (s, 3 H, CH$_3$), 1.60 (s, 3 H, CH$_3$).



2

(2)

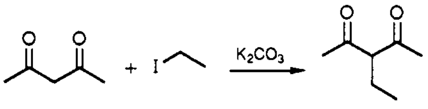
Diethyl Oximidomalonate (2). Diethyl malonate (69.2 g) was dissolved in 98 mL of glacial HOAc and cooled to 0 °C in an ice/salt bath. A solution of 29.62 g of NaNO$_2$ in 39.5 mL of H$_2$O was slowly added so as to maintain the reaction temperature at 0 °C throughout the addition. After this addition, two more separate NaNO$_2$ solutions (29.62 g in 39.5 mL of H$_2$O) were added. The temperature was carefully maintained at 0 °C throughout the ~4-h addition. The reaction mixture was allowed to warm to room temperature and was then stirred for 16 h. Dry Et$_2$O (100 mL) was added, and the organic layer was separated. This layer was washed first with H$_2$O, then with saturated NaHCO$_3$ until the washings were alkaline, and finally washed again with H$_2$O. The organic layer was separated and placed on a Rotovap for 1 h at 80 °C to remove Et$_2$O, DEM, and H$_2$O to yield 65.61 g (80%) of **2**: ^{1}H NMR (CDCl$_3$) δ 4.30 (q, 4 H, CH_2CH$_3$), 1.28 (t, 6 H, CH$_2$CH_3).



1 2 3

(3)

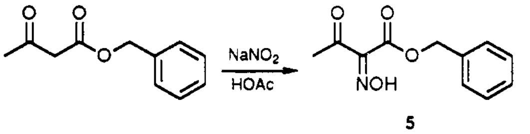
2-(Ethoxycarbonyl)-3,4-dimethylpyrrole (3). Glacial HOAc (114 mL) was placed in a 1-L round-bottom flask and heated to 85 °C. NaOAc (31.09 g), 27.54 g of **1**, 37.20 g of **2**, and a solution of 47 mL of HOAc in 19.6 mL of H$_2$O were then added sequentially. The reaction temperature was raised to 95 °C, and 43.26 g of Zn dust was added over 45 min while maintaining the temperature between 95 and 110 °C. After the addition was complete, the mixture was heated and stirred for 45 min longer. The reaction was then poured into 500 mL of ice H$_2$O, filtered, and washed with H$_2$O. The solid was subsequently dissolved in CH$_2$Cl$_2$, washed with saturated NaHCO$_3$, and dried, and then the solvent was removed under reduced pressure. The crude pyrrole was chromatographed on silica with CH$_2$Cl$_2$ to yield 6.68 g (18%) of **3**: ^{1}H NMR (CDCl$_3$) δ 8.70 (br s, 1 H, NH), 6.60 (s, 1 H, αH), 4.27 (q, 2 H, CH_2CH$_3$), 2.22 (s, 3 H, CH$_3$), 1.96 (s, 3 H, CH$_3$), 1.31 (t, 3 H, CH$_2$CH_3).



4

(4)

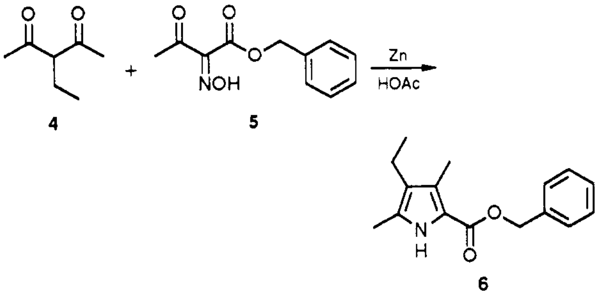
3-Ethyl-2,4-pentanedione (4). Iodoethane (45 mL), 55 mL of acetone, and 50 mL of 2,4-pentanedione were added to a 250-mL round-bottom flask containing 84 g of K$_2$CO$_3$. The mixture was then refluxed for 24 h. The solids were filtered off and washed with acetone. Solvents were removed by evaporation, and the residue was distilled at reduced pressure to yield 45.29 g (35%) of **4**: ^{1}H NMR (CDCl$_3$) δ 2.04 (s, 6 H, CH$_3$), 1.78 (q, 2 H, CH_2CH$_3$), 0.80 (t, 3 H, CH$_2$CH_3). The ^{1}H NMR spectrum shows the enol form as well.



5

(5)

Benzyl Acetyloximidoacetate (5). Benzyl acetoacetate (74.74 g) and 140 mL of glacial HOAc were placed in a 1-L flask and cooled in an ice bath. A solution of 27.18 g of NaNO$_2$ in 36 mL of H$_2$O was added slowly so as to maintain a temperature of 15 °C. The reaction mixture was then warmed to 25 °C and stirred for 1 h. The solution was used immediately in the pyrrole synthesis.



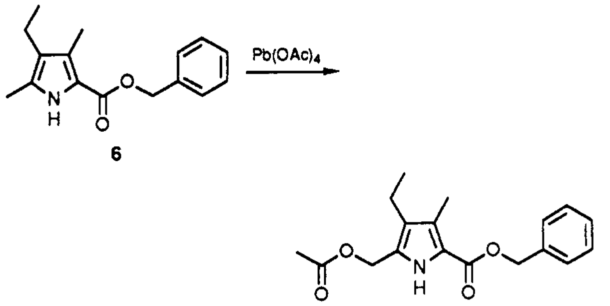
6

(6)

---

(14) Cane, R.; Marcus, R.; Siders, P. *J. Phys. Chem.* **1986**, *90*, 1436.

2-(Benzyloxycarbonyl)-3,5-dimethyl-4-ethylpyrrole (6). Na_2CO_3 (19.32 g) was dissolved in 120 mL of glacial HOAc in a 1-L flask. **4** (50 g) was then added with stirring. The oximine solution, **5**, was then added dropwise along with 59.2 g of Zn dust while maintaining the temperature between 60 and 65 °C. The reaction was heated to 85 °C for 2 h and then poured into 1 L of H_2O while still hot. The mixture was allowed to stand overnight, after which it was filtered and washed with H_2O. The solid was dissolved in CH_2Cl_2, filtered, and dried with Na_2SO_4, and the solvent was then removed under reduced pressure. The crude pyrrole was crystallized from EtOH to yield 39.5 g (39%) of **6**: ^1H NMR ($CDCl_3$) δ 8.55 (br s, 1 H, NH), 7.2–7.4 (m, 5 H, Ar), 5.24 (s, 2 H, CH_2), 2.33 (q, 2 H, CH_2CH_3), 2.24 (s, 3 H, CH_3), 2.14 (s, 3 H, CH_3), 1.01 (t, 3 H, CH_2CH_3).

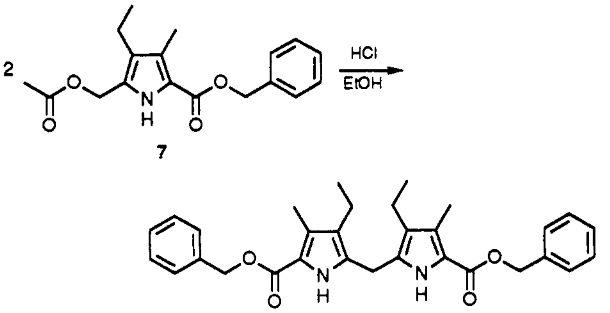


6

(7)

7

2-(Benzyloxycarbonyl)-3-methyl-4-ethyl-5-(acetoxymethyl)pyrrole (7). **6** (10.05 g) was dissolved in 245 mL of glacial HOAc in a 500-mL round-bottom flask. Ac_2O (21.9 mL) was added along with 19.67 g of $Pb(OAc)_4$. The reaction mixture was stirred overnight and then poured into 1 L of H_2O. The white solid was filtered and washed with H_2O. The solid was then dissolved in CH_2Cl_2, and $NaHCO_3$ and Na_2SO_4 were added. The mixture was filtered and the solvent removed under reduced pressure. The crude pyrrole was recrystallized from CH_2Cl_2/hexanes to yield 6.89 g (56%) of **7**: ^1H NMR ($CDCl_3$) δ 8.92 (br s, 1 H, NH), 7.2–7.4 (m, 5 H, Ar), 5.25 (s, 2 H, CH_2Ar), 4.96 (s, 2 H, CH_2OAc), 2.41 (q, 2 H, CH_2CH_3), 2.24 (s, 3 H, CH_3), 2.01 (s, 3 H, CH_3), 1.02 (t, 3 H, CH_2CH_3).

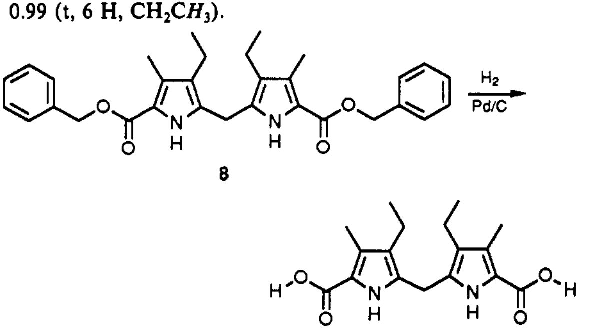


7

(8)

8

5,5′-Bis(benzyloxycarbonyl)-3,3′-diethyl-4,4′-dimethyl-2,2′-dipyrrylmethane (8). **7** (8.10 g) was dissolved with heating in 200 mL of EtOH and placed under N_2. HCl (5 mL) was added, and the solution was refluxed for 1 h. Solvent was removed until crystallization commenced, at which point the flask was refrigerated. The crystals were filtered, washed with cold EtOH, and dried to yield 5.07 g (40%) of **8**: ^1H NMR ($CDCl_3$) δ 8.66 (br s, 2 H, NH), 7.2–7.4 (m, 10 H, Ar), 5.20 (s, 4 H, CH_2Ar), 3.78 (s, 2 H, CH_2), 2.37 (q, 4 H, CH_2CH_3), 2.22 (s, 6 H, CH_3), 0.99 (t, 6 H, CH_2CH_3).

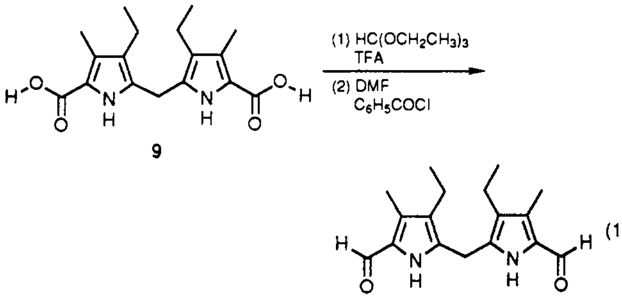


8

(9)

9

5,5′-Dicarboxy-3,3′-diethyl-4,4′-dimethyl-2,2′-dipyrrylmethane (9). **8** (4.00 g) was dissolved in 100 mL of EtOAc, and 0.4 g of 10% palladium on activated carbon was added. The flask was placed under H_2, and the mixture was stirred at room temperature for 21 h. The catalyst was removed by filtration, and then the solvent was removed under reduced pressure. The solid was dried under vacuum and used without further purification (2.2 g, 86%).

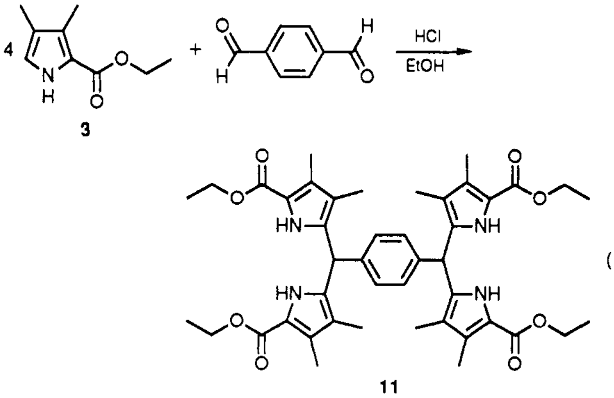


9

(10)

10

5,5′-Diformyl-3,3′-diethyl-4,4′-dimethyl-2,2′-dipyrrylmethane (10). This compound was synthesized by two different methods. (1) **9** (2.78 g) was heated in 8 mL of trifluoroacetic acid to 50 °C and stirred for 2 min. The solution was then cooled to 0 °C, and 2.4 mL of triethyl orthoformate was added. The reaction mixture was stirred at 0 °C for 5 min before being poured into 160 mL of H_2O. The solid was filtered and then added to a solution of 20 mL of absolute EtOH and 40 mL of 1 M NH_4OH and stirred at room temperature for 10 min. The solid was filtered and then crystallized from $CHCl_3$/petroleum ether to yield 1.27 g (51%) of **10**. (2) **9** (1.57 g) was dissolved in 5.64 mL of DMF and heated to reflux under N_2 for 30 min. The reaction was then cooled to 0 °C in an ice/salt bath, and 1.88 mL of benzoyl chloride was added dropwise. The reaction was stirred for 15 min, and 9.4 mL of benzene was added. The reaction was allowed to warm to room temperature and then stirred for 1 h, after which it was filtered and the solid was washed with benzene. The wet filtercake was dissolved in 31.3 mL of EtOH/H_2O (50%) containing 1.80 g of Na_2CO_3. The benzene was removed as the H_2O azeotrope, and 31.3 mL of H_2O was added to dissolve the remaining Na_2CO_3. The mixture was stirred for 8 h, filtered, washed with H_2O, and dried. The product was crystallized from EtOH as tan needles to yield 0.94 g (67%) of **10**: ^1H NMR ($CDCl_3$) δ 10.55 (br s, 2 H, NH), 9.48 (s, 2 H, COH), 3.95 (s, 2 H, CH_2), 2.46 (q, 4 H, CH_2CH_3), 2.29 (s, 6 H, CH_3), 1.07 (t, 6 H, CH_2CH_3).

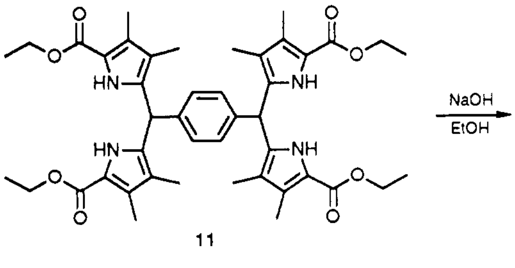


3

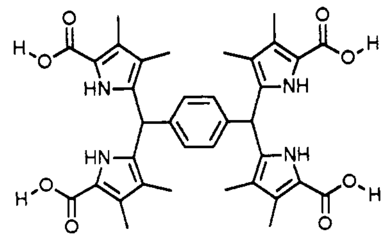
(11)

11

1,4-Bis[3,3′,4,4′-tetramethyl-5,5′-bis(ethoxycarbonyl)-2,2′-dipyrrylmethyl]benzene (11). 1,4-Diformylbenzene (0.100 g) and 0.499 g of **3** were dissolved with heating in 5 mL of absolute EtOH. The reaction mixture was then heated to reflux, and 0.12 mL of HCl was added. The reaction was placed under N_2 and refluxed for 1 h. Upon cooling, the product crystallized. It was filtered, washed with cold EtOH, and dried to yield 0.483 g (84%) of **11**: ^1H NMR ($CDCl_3$) δ 8.23 (br s, 4 H, NH), 7.00 (s, 4 H, Ar), 5.44 (s, 2 H, CH), 4.20 (q, 8 H, CH_2CH_3), 2.20 (s, 12 H, CH_3), 1.75 (s, 12 H, CH_3), 1.26 (t, 12 H, CH_2CH_3).



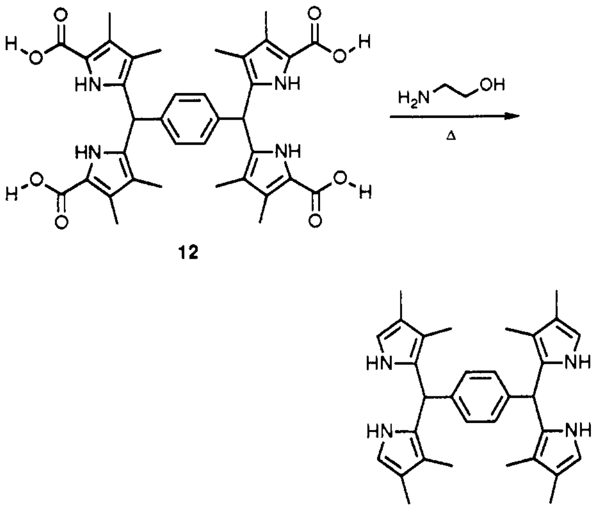
11



(12)

12

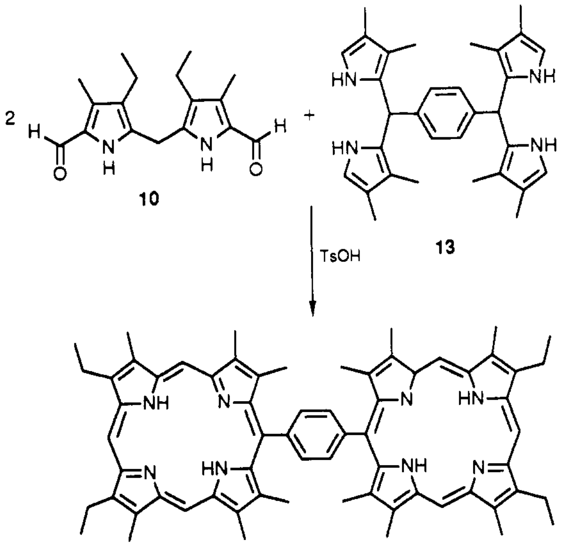
1,4-Bis(3,3′,4,4′-tetramethyl-5,5′-dicarboxy-2,2′-dipyrrylmethyl)benzene (12). **11** (0.750 g) was suspended in 10.5 mL of absolute EtOH and brought to reflux. A total of 1.30 mL of 5 M NaOH solution was added, and the reaction mixture was refluxed for 18 h under N_2. The EtOH was removed under reduced pressure, and the residue was diluted with 8.6 mL of H_2O and filtered. The filtrate was acidified with glacial HOAc, and the tetraacid was precipitated as a pink solid. The solid was dried in vacuo and used without further purification (0.578 g, 90%).



13

(13)

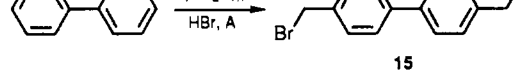
1,4-Bis(3,3′,4,4′-tetramethyl-2,2′-dipyrrylmethyl)benzene (13). **12** (0.578 g) was dissolved in 8.6 g of degassed ethanolamine. The mixture was placed under N_2 and refluxed for 1 h, after which the reaction mixture was poured into 40 mL of ice H_2O while still warm. A solid soon separated, which was filtered and dried to yield 0.4033 g (95%) of **13**: ^{1}H NMR ($CDCl_3$) δ 7.25 (br s, 4 H, NH), 7.02 (s, 4 H, Ar), 6.32 (s, 4 H, αH), 5.39 (s, 2 H, CH), 1.98 (s, 12 H, CH_3), 1.74 (s, 12 H, CH_3).



(14)

14

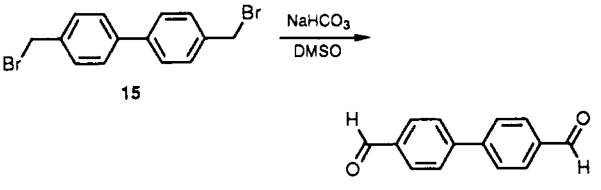
1,4-Bis(1,8-diethyl-2,3,4,5,6,7-hexamethylporphyrinyl)benzene (14). **13** (0.0836 g) was dissolved in 42 mL of dry CH_2Cl_2, and then 0.100 g of **10** in 28 mL of dry CH_2Cl_2 was added. The reaction was carefully protected from light by wrapping the flask in aluminum foil. TsOH·H_2O (0.510 g) in 8.2 mL of dry CH_3OH was added, and the reaction was stirred at room temperature for 6 h in air. Saturated $Zn(OAc)_2$ (8.2 mL) in dry CH_3OH was then added, and the reaction mixture was stirred overnight. The reaction mixture was washed sequentially with H_2O, then saturated $NaHCO_3$, and with H_2O again. The organic layer was then dried with Na_2SO_4, and the solvent was removed under reduced pressure. It was then chromatographed on silica (CH_2Cl_2), and the porphyrin bands were collected. The Zn was removed with trifluoroacetic acid. The mixture of porphyrins were then rechromatographed on silica (CH_2Cl_2/1% CH_3OH). The slow-moving bands were chromatographed on alumina (1:5, EtOAc/hexanes) to yield 0.0051 g (3%) of **14**: ^{1}H NMR ($CDCl_3$) δ 10.13 (s, 4 H, $\alpha + \gamma$ meso), 9.93 (s, 2 H, β meso), 8.23 (s, 4 H, Ar), 4.23 (q, 8 H, CH_2CH_3), 3.60 (s, 12 H, CH_3), 3.49 (s, 12 H, CH_3), 2.38 (s, 12 H, CH_3), 1.82 (t, 12 H, CH_2CH_3), −3.20 (br s, 2 H, NH), −3.34 (br s, 2 H, NH); MS *m/e* 975.4444 (975.4445 calcd).



(15)

15

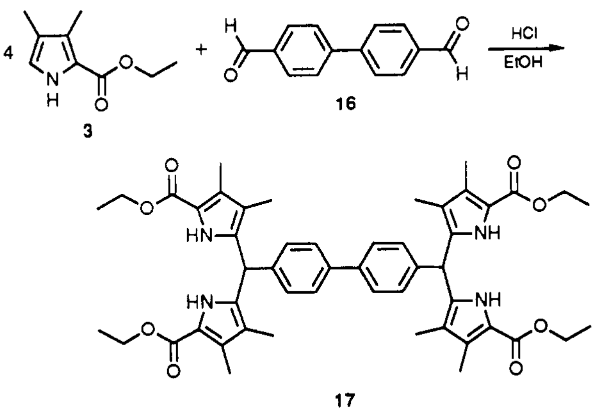
4,4′-Bis(bromomethyl)-1,1′-biphenyl (15). Biphenyl (20.02 g) and 15.5 g of paraformaldehyde were placed in a 500-mL round-bottom flask, and 45.24 mL of 48% HBr, 25.88 mL of 85% H_3PO_4, and 51.72 mL of 33% HBr in HOAc were then added. The mixture was heated to 80 °C for 1 h under N_2. The temperature was then raised to 120 °C for 5 h, after which the reaction was cooled to room temperature. The solids were filtered, washed with hexanes, and then crystallized from benzene/hexanes to yield 13.7 g (31%) of **15**: ^{1}H NMR ($CDCl_3$) δ 7.57 (d, 4 H, Ar), 7.46 (d, 4 H, Ar), 4.75 (s, 4 H, CH_2).



(16)

16

4,4′-Diformyl-1,1′-biphenyl (16). **15** (6.02 g) and 24.8 g of $NaHCO_3$ were placed in a 500-mL round-bottom flask, and 186 mL of DMSO was added. The reaction was heated to 115 °C under N_2 for 3.5 h. The reaction mixture was allowed to cool to room temperature and then was poured into 250 mL of H_2O. The precipitate was filtered, dissolved in CH_2Cl_2, washed with H_2O, and dried, and the solvent was removed under reduced pressure. The crude aldehyde was chromatographed on silica (CH_2Cl_2) to yield 1.85 g (50%) of **16**: ^{1}H NMR ($CDCl_3$) δ 10.08 (s, 2 H, COH), 8.00 (d, 4 H, Ar), 7.80 (d, 4 H, Ar); mp 165–168 °C dec.



(17)

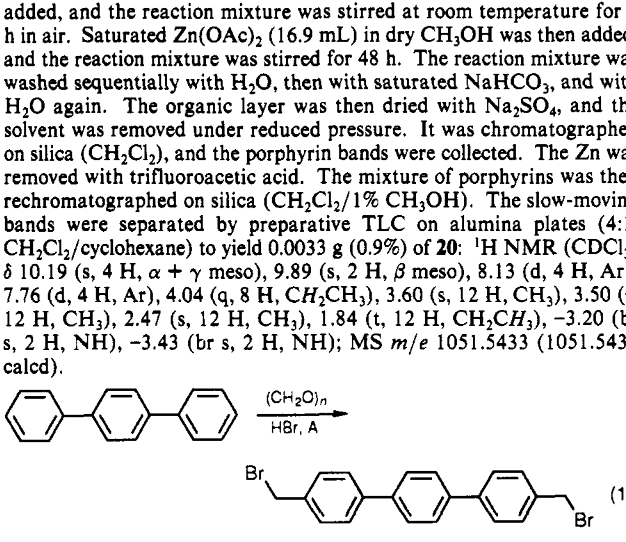
17

4,4′-Bis[3,3′,4,4′-tetramethyl-5,5′-bis(ethoxycarbonyl)-2,2′-dipyrrylmethyl]-1,1′-biphenyl (17). **16** (0.4222 g) and 1.3429 g of **3** were heated in 13.5 mL of absolute EtOH until both dissolved. The reaction mixture was placed under N_2, and 0.32 mL of HCl was added. After the reaction refluxed for 1 h, the mixture was cooled and the product crystallized. The crystals were filtered and washed with cold EtOH to yield 1.384 g (82%) of **17**: ^{1}H NMR ($CDCl_3$) δ 8.23 (br s, 4 H, NH), 7.49 (d, 4 H, Ar), 7.10 (d, 4 H, Ar), 5.49 (s, 2 H, CH), 4.22 (q, 8 H, CH_2CH_3), 2.21 (s, 12 H, CH_3), 1.76 (s, 12 H, CH_3), 1.27 (t, 12 H, CH_2CH_3); mp 215–217 °C dec.

4,4′-Bis(3,3′,4,4′-tetramethyl-5,5′-dicarboxy-2,2′-dipyrrylmethyl)-1,1′-biphenyl (18). (See reaction 12.) **17** (1.3327 g) was suspended in 17 mL of absolute EtOH and brought to reflux. A 5 M NaOH solution (2.1 mL) was added, and the reaction mixture was refluxed for 16 h under N_2. The EtOH was removed under reduced pressure, and the residue was dissolved in H_2O and filtered. The filtrate was slowly acidified with 1 M HOAc. The pink precipitate was washed with H_2O and then dried in vacuo and used without further purification: 0.9588 g (83%).

4,4′-Bis(3,3′,4,4′-tetramethyl-2,2′-dipyrrylmethyl)-1,1′-biphenyl (19). (See reaction 13.) **18** (0.9588 g) was dissolved in 17.3 mL of degassed ethanolamine. The solution was placed under N_2 and refluxed for 1 h, after which the reaction mixture was poured into 75 mL of H_2O while still warm. A solid soon separated, which was filtered and dried to yield 0.6895 g (95%) of **19**: ^{1}H NMR ($CDCl_3$) δ 7.47 (d, 4 H, Ar), 7.27 (br s, 4 H, NH), 7.13 (d, 4 H, Ar), 6.36 (s, 4 H, αH), 5.46 (s, 2 H, CH), 1.98 (s, 12 H, CH_3), 1.87 (s, 12 H, CH_3).

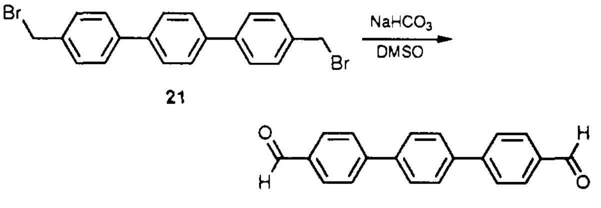
4,4′-Bis(1,8-diethyl-2,3,4,5,6,7-hexamethylporphyrinyl)-1,1′-biphenyl (20). (See reaction 14.) **19** (0.2003 g) was dissolved in 85.6 mL of dry CH_2Cl_2, and then 0.2069 g of **10** in 60 mL of dry CH_2Cl_2 was added. The reaction was carefully protected from light by wrapping the flask in aluminum foil. TsOH·H_2O (1.06 g) in 16.9 mL of dry CH_3OH was added, and the reaction mixture was stirred at room temperature for 6 h in air. Saturated $Zn(OAc)_2$ (16.9 mL) in dry CH_3OH was then added, and the reaction mixture was stirred for 48 h. The reaction mixture was washed sequentially with H_2O, then with saturated $NaHCO_3$, and with H_2O again. The organic layer was then dried with Na_2SO_4, and the solvent was removed under reduced pressure. It was chromatographed on silica (CH_2Cl_2), and the porphyrin bands were collected. The Zn was removed with trifluoroacetic acid. The mixture of porphyrins was then rechromatographed on silica (CH_2Cl_2/1% CH_3OH). The slow-moving bands were separated by preparative TLC on alumina plates (4:1, CH_2Cl_2/cyclohexane) to yield 0.0033 g (0.9%) of **20**: ^{1}H NMR ($CDCl_3$) δ 10.19 (s, 4 H, $\alpha + \gamma$ meso), 9.89 (s, 2 H, β meso), 8.13 (d, 4 H, Ar), 7.76 (d, 4 H, Ar), 4.04 (q, 8 H, CH_2CH_3), 3.60 (s, 12 H, CH_3), 3.50 (s, 12 H, CH_3), 2.47 (s, 12 H, CH_3), 1.84 (t, 12 H, CH_2CH_3), −3.20 (br s, 2 H, NH), −3.43 (br s, 2 H, NH); MS *m/e* 1051.5433 (1051.5433 calcd).



(18)

21

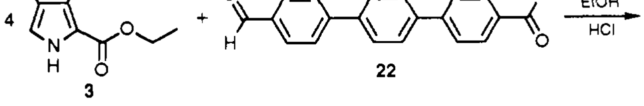
4,4″-Bis(bromomethyl)-*p*-terphenyl (21). *p*-Terphenyl (5.00 g) and 2.90 g of paraformaldehyde were placed in a 100-mL round-bottom flask, and 19.76 mL of 33% HBr in HOAc and 4.35 mL of H_3PO_4 were then added. The mixture was heated to 80 °C for 18 h under N_2. The temperature was raised to 125 °C for 5 h, after which the reaction was cooled to room temperature. The solids were filtered and washed with acetone. They were then repeatedly extracted with boiling benzene. The hot benzene solution was filtered and the product crystallized by adding hexanes to yield 0.61 g (6.7%) of **21**: ^{1}H NMR ($CDCl_3$) δ 7.68 (s, 4 H, Ar), 7.62 (d, 4 H, Ar), 7.50 (d, 4 H, Ar), 4.58 (s, 4 H, CH_2).

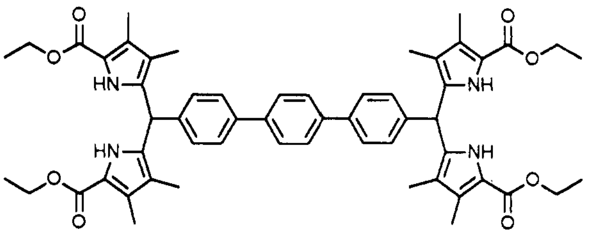


(19)

22

4,4″-Diformyl-*p*-terphenyl (22). **21** (0.6044 g) and 2.03 g of $NaHCO_3$ were placed in a 50-mL round-bottom flask, and 15.3 mL of DMSO was added. The reaction was heated to 115 °C under N_2 for 3.5 h. The reaction was then allowed to cool to room temperature, after which it was poured into 25 mL of H_2O. The precipitate was filtered, dissolved in CH_2Cl_2, washed with H_2O, and dried, and the solvent was removed under reduced pressure. The crude aldehyde was chromatographed on silica (CH_2Cl_2) to yield 0.1180 g (28%) of **22**: ^{1}H NMR ($CDCl_3$) δ 10.16 (s, 2 H, COH), 8.00 (d, 4 H, Ar), 7.82 (d, 4 H, Ar), 7.79 (s, 4 H, Ar); mp 185 °C dec.





(20)

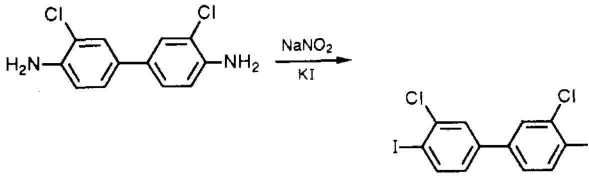
23

4,4″-Bis[3,3′,4,4′-tetramethyl-5,5′-bis(ethoxycarbonyl)-2,2′-dipyrrylmethyl]-*p*-terphenyl (23). **22** (0.0987 g) and 0.2305 g of **3** were heated in 2.3 mL of absolute EtOH until both dissolved. The reaction mixture was refluxed under N_2, and 0.055 mL of HCl was added. The mixture was refluxed for 1 h. The solution was allowed to cool to room temperature, after which it was cooled in a freezer to 0 °C. The product precipitated as a white solid, which was filtered, washed with 70% aqueous EtOH, and dried to yield 0.2766 g (87%) of **23**: ^{1}H NMR ($CDCl_3$) δ 8.27 (br s, 4 H, NH), 7.66 (s, 4 H, Ar), 7.60 (d, 4 H, Ar), 7.17 (d, 4 H, Ar), 5.54 (s, 2 H, CH), 4.26 (q, 8 H, CH_2CH_3), 2.26 (s, 12 H, CH_3), 1.80 (s, 12 H, CH_3), 1.32 (t, 12 H, CH_2CH_3); mp 172–173 °C dec.

4,4″-Bis(3,3′,4,4′-tetramethyl-5,5′-dicarboxy-2,2′-dipyrrylmethyl)-*p*-terphenyl (24). (See reaction 12.) **23** (0.2714 g) was suspended in 3.2 mL of absolute EtOH and brought to reflux. A 5 M NaOH solution (0.39 mL) was added, and the reaction mixture was refluxed for 18 h under N_2. The EtOH was removed under reduced pressure, and the residue was suspended in 25 mL of H_2O and slowly acidified with 1 M HOAc. The pink solid was filtered, washed with H_2O, dried in vacuo, and then used without further purification: 0.25 g (100%).

4,4″-Bis(3,3′,4,4′-tetramethyl-2,2′-dipyrrylmethyl)-*p*-terphenyl (25). (See reaction 13.) **24** (0.2520 g) was dissolved in 3.7 mL of degassed ethanolamine. The solution was placed under N_2 and refluxed for 1 h, after which the reaction mixture was poured into 40 mL of ice H_2O while still warm. The product precipitated as a tan solid, which was filtered, washed with H_2O, and dried to yield 0.1892 g (96%) of **25**: ^{1}H NMR ($CDCl_3$) δ 7.64 (s, 4 H, Ar), 7.61 (d, 4 H, Ar), 7.27 (br s, 4 H, NH), 7.20 (d, 4 H, Ar), 6.33 (s, 4 H, αH), 5.50 (s, 2 H, CH), 2.00 (s, 12 H, CH_3), 1.90 (s, 12 H, CH_3).

4,4″-Bis(1,8-diethyl-2,3,4,5,6,7-hexamethylporphyrinyl)-*p*-terphenyl (26). (See reaction 14.) **25** (0.1117 g) was dissolved in 26.6 mL of dry CH_2Cl_2, and then 0.1014 g of **10** in 18.6 mL of dry CH_2Cl_2 was added. The reaction was carefully protected from light by wrapping the flask in aluminum foil. TsOH·H_2O (0.33 g) in 5.2 mL of dry CH_3OH was added, and the reaction mixture was stirred at room temperature for 6 h in air. Saturated $Zn(OAc)_2$ (5.2 mL) in dry CH_3OH was then added, and the reaction mixture was stirred for 48 h. The reaction mixture was washed sequentially with H_2O, then saturated $NaHCO_3$, and washed with H_2O again. The organic layer was then dried with Na_2SO_4, and the solvent was removed under reduced pressure. Chromatography was performed on silica (CH_2Cl_2) and the porphyrin bands were collected. The Zn was removed with trifluoroacetic acid. The mixture of porphyrins was then rechromatographed on silica (CH_2Cl_2/1% CH_3OH). The slow-moving bands were separated by preparative TLC on alumina plates (4:1 CH_2Cl_2/cyclohexane) to yield 0.0014 g (0.7%) of **26**: ^{1}H NMR ($CDCl_3$) δ 10.17 (s, 4 H, $\alpha + \gamma$ meso), 9.96 (s, 2 H, β meso), 8.18 (d, 4 H, Ar), 8.13 (s, 4 H, Ar), 8.05 (d, 4 H, Ar), 4.07 (q, 8 H, CH_2CH_3), 3.65 (s, 12 H, CH_3), 3.54 (s, 12 H, CH_3), 2.52 (s, 12 H, CH_3), 1.88 (t, 12 H, CH_2CH_3), −3.17 (br s, 2 H, NH), −3.10 (br s, 2 H, NH); MS *m/e* 1127.6422 (1127.6421 calcd).

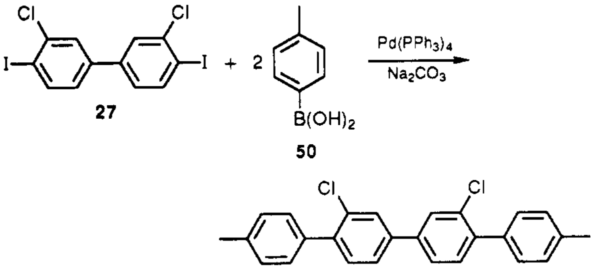


(21)

27

4,4′-Diiodo-3,3′-dichloro-1,1′-biphenyl (27). 3,3′-Dichlorobenzidine (25 g) was placed in a 600-mL beaker, and 55 mL of HCl was added. The mixture was stirred and cooled in an ice/salt bath to 0 °C. Ice (50 g) was added and then, very slowly, 11.94 g of $NaNO_2$ in 48.5 mL of H_2O was added. The temperature was maintained below 5 °C throughout the addition. After the addition was complete, the reaction mixture was stirred for 15 min and then poured though a glass wool plug into a 3-L beaker containing 88.16 g of KI in 294 mL of H_2O. The mixture was then stirred at room temperature overnight, after which it was extracted with ether, washed with 10% NaOH, 5% $NaHSO_3$, and

H_2O, and dried with Na_2SO_4, and the solvent was removed under reduced pressure to yield 33.25 g (71%) of **27**: ^{1}H NMR ($CDCl_3$) δ 7.90 (d, 2 H, Ar), 7.61 (s, 2 H, Ar), 7.12 (d, 2 H, Ar).

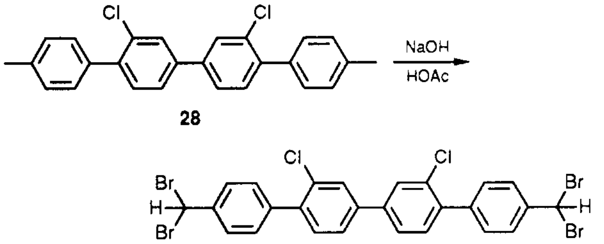


27

50

28 (22)

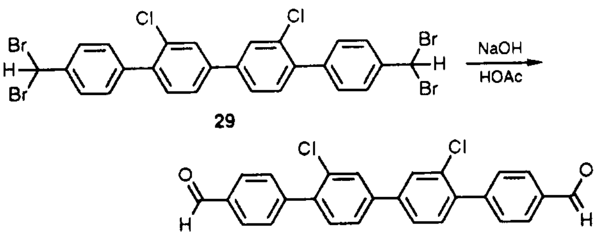
4,4‴-Dimethyl-3′,3″-dichloro-*p*-quaterphenyl (28). **27** (8 g) and 60 mL of benzene were placed in a 250-mL round-bottom flask. $Pd(PPh_3)_4$ (1.00 g) was added followed by 34 mL of 2 M Na_2CO_3. **50** (5.25 g) in 15 mL of absolute EtOH was added, and the mixture was refluxed under N_2 with rapid stirring overnight. After the reaction had cooled, 2 mL of H_2O_2 (30%) was added and the mixture was stirred for 1 h. The reaction mixture was extracted with ether, washed with brine, and dried, and the solvent was removed under reduced pressure. The product was chromatographed on silica (50% CCl_4/hexanes) to yield 3.8 g (56%) of **28** as a yellow powder: ^{1}H NMR ($CDCl_3$) δ 7.74 (s, 2 H, Ar), 7.56 (d, 2 H, Ar), 7.44 (d, 2 H, Ar), 7.41 (d, 4 H, Ar), 7.29 (d, 4 H, Ar), 2.44 (s, 6 H, CH_3).



28

29 (23)

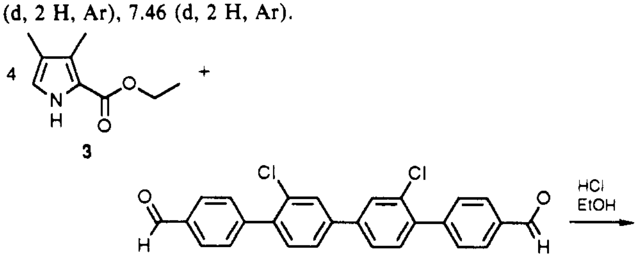
4,4‴-Bis(dibromomethyl)-3′,3″-dichloro-*p*-quaterphenyl (29). **28** (3.38 g) and 200 mL of CCl_4 were placed in a 500-mL round-bottom flask. NBS (6.72 g) and a few crystals of benzoyl peroxide were added, and the reaction was refluxed for 20 h. The mixture was filtered hot, and the solids were washed with CCl_4. The solvent was removed, and the product was used without further purification.



29

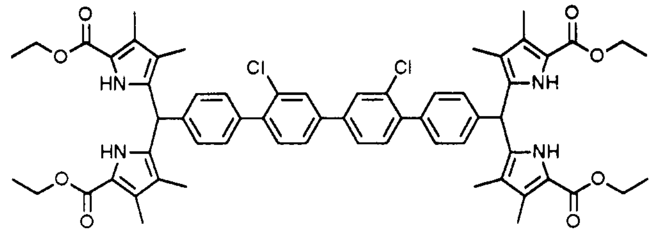
30 (24)

4,4‴-Diformyl-3′,3″-dichloro-*p*-quaterphenyl (30). Crude **29** (6 g) was dissolved in 300 mL of HOAc containing 6 g of NaOH. The reaction was refluxed for 3 h under N_2 and then poured into 600 mL of H_2O. It was then extracted with CH_2Cl_2 and dried with Na_2SO_4, and the solvent was removed under reduced pressure. The resulting precipitate was dissolved in CH_3OH, and 0.5 g of K_2CO_3 was added. The mixture was stirred for 30 min, after which the solvent was removed and the crude dialdehyde was chromatographed on silica (CH_2Cl_2) to yield 1.00 g (28%) of **30** as a white powder: ^{1}H NMR ($CDCl_3$) δ 10.10 (s, 2 H, COH), 8.30 (d, 4 H, Ar), 7.76 (s, 2 H, Ar), 7.68 (d, 4 H, Ar), 7.60 (d, 2 H, Ar), 7.46 (d, 2 H, Ar).



3

30



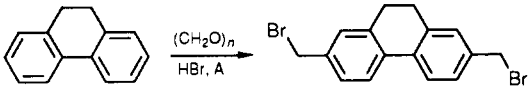
31 (25)

4,4‴-Bis[3,3′,4,4′-tetramethyl-5,5′-bis(ethoxycarbonyl)-2,2′-dipyrrylmethyl]-3′,3″-dichloro-*p*-quaterphenyl (31). **30** (0.75 g) and 1.16 g of **3** were heated in 12.0 mL of absolute EtOH until both dissolved. The mixture was placed under N_2, and 0.28 mL of HCl was added. The mixture was refluxed for 1 h. The reaction was cooled to room temperature and the product precipitated as a light pink solid. The solid was filtered, washed with 70% EtOH, and dried to yield 1.75 g (96%) of **31**: ^{1}H NMR ($CDCl_3$) δ 8.62 (br s, 4 H, NH), 7.72 (s, 2 H, Ar), 7.56 (d, 2 H, Ar), 7.45 (d, 4 H, Ar), 7.20 (d, 2 H, Ar), 7.17 (d, 4 H, Ar), 5.60 (s, 2 H, CH), 4.23 (q, 8 H, $C\mathit{H}_2CH_3$), 2.27 (s, 12 H, CH_3), 1.86 (s, 12 H, CH_3), 1.30 (t, 12 H, $CH_2C\mathit{H}_3$).

4,4‴-Bis(3,3′,4,4′-tetramethyl-5,5′-dicarboxy-2,2′-dipyrrylmethyl)-3′,3″-dichloro-*p*-quaterphenyl (32). (See reaction 12.) **31** (1.65 g) was suspended in 18.6 mL of absolute EtOH and brought to reflux. A 5 M NaOH solution (2.3 mL) was added and the mixture was refluxed for 18 h under N_2. The EtOH was removed under reduced pressure, and the residue was dissolved in H_2O and then filtered. The filtrate was slowly acidified with 1 M HOAc. The precipitate was filtered, washed with H_2O, and dried in vacuo. The product was used without further purification, 1.4 g (94%).

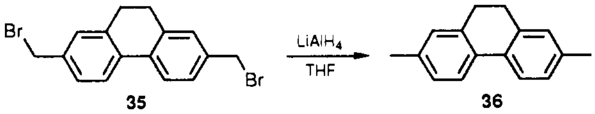
4,4‴-Bis(3,3′,4,4′-tetramethyl-2,2′-dipyrrylmethyl)-3′,3″-dichloro-*p*-quaterphenyl (33). (See reaction 13.) **32** (1.00 g) was dissolved in 10.9 mL of degassed ethanolamine. The solution was placed under N_2 and refluxed for 1 h, after which it was poured into 52 mL of ice H_2O while still warm. A gold solid soon separated, which was filtered, washed with H_2O, and dried in vacuo to yield 0.63 g (77%) of **33**. Caution must be taken with this reaction to maintain an inert atmosphere throughout the experimental procedure. **33**: ^{1}H NMR ($CDCl_3$) δ 7.74 (s, 2 H, Ar), 7.58 (d, 2 H, Ar), 7.46 (d, 6 H, Ar), 7.37 (br s, 4 H, NH), 7.22 (d, 4 H, Ar), 6.42 (s, 4 H, αH), 5.57 (s, 2 H, CH), 2.06 (s, 12 H, CH_3), 1.87 (s, 12 H, CH_3).

4,4‴-Bis(1,8-diethyl-2,3,4,5,6,7-hexamethylporphyrinyl)-3′,3″-dichloro-*p*-quaterphenyl (34). **33** (0.3000 g) was dissolved in 93 mL of dry CH_2Cl_2, and then 0.2222 g of **10** in 64 mL of dry CH_2Cl_2 was added. The reaction was carefully protected from light by wrapping the flask in aluminum foil. TsOH·H_2O (1.1220 g) in 18 mL of dry CH_3OH was added, and the reaction was stirred at room temperature for 6 h in air. Saturated $Zn(OAc)_2$ (18 mL) in dry CH_3OH was then added, and the reaction mixture was stirred for 60 h. The reaction mixture was washed sequentially with H_2O, then with saturated $NaHCO_3$, and with H_2O again. The organic layer was then dried with Na_2SO_4, and the solvent was removed under reduced pressure. It was then chromatographed on silica (CH_2Cl_2), and the porphyrin bands were collected. The Zn was removed with trifluoroacetic acid. The mixture of porphyrins was then rechromatographed on silica (CH_2Cl_2/1% CH_3OH). The product decomposes in the purification process.



35 (26)

2,7-Bis(bromomethyl)-9,10-dihydrophenanthrene (35). 9,10-Dihydrophenanthrene (10.52 g) and 7.70 g of paraformaldehyde were placed in a 200-mL round-bottom flask, and 20.16 mL of 48% HBr, 11.53 mL of 85% H_3PO_4, and 23.04 mL of 33% HBr in HOAc were added. The mixture was heated to 80 °C under N_2 for 23 h. The temperature was then increased to 120 °C for 5 h, after which the reaction was cooled to room temperature and a solid soon separated. It was filtered, washed with acetone, and then crystallized from benzene/hexanes to yield 11.74 g (55%) of **35**: ^{1}H NMR ($CDCl_3$) δ 7.70 (d, 2 H, Ar), 7.33 (d, 2 H, Ar), 7.26 (s, 2 H, Ar), 4.52 (s, 4 H, CH_2Br), 2.86 (s, 4 H, CH_2); mp 150–151 °C.

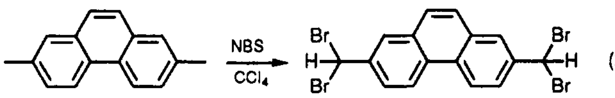


35 36 (27)

2,7-Dimethyl-9,10-dihydrophenanthrene (36). **35** (7.00 g) was dissolved in 50 mL of dry THF and placed under N_2. $LiAlH_4$ (1.5 g) was cautiously added, and the suspension was stirred at room temperature for 40 h. A concentrated NaOH solution was added dropwise until vigorous H_2 evolution ceased, and the reaction mixture was then stirred for 30 min. $MgSO_4$ was added and the solution was filtered. The solids were washed well with Et_2O. The filtrate was evaporated, the solids were dissolved in CH_2Cl_2 and filtered again to remove trace LiBr, and the solvent was removed under reduced pressure to yield 3.50 g (88%) of **36**: ^{1}H NMR ($CDCl_3$) δ 7.62 (d, 2 H, Ar), 7.11 (d, 2 H, Ar), 7.04 (s, 2 H, Ar), 2.82 (s, 4 H, CH_2), 2.38 (s, 6 H, CH_3).

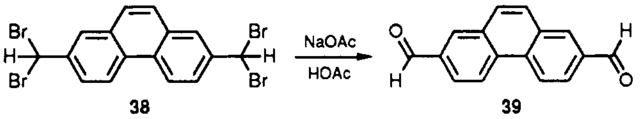
(28)

2,7-Dimethylphenanthrene (37). **36** (3.50 g) was dissolved in 50 mL of dry benzene, and 4.20 g of DDQ was added. The reaction was refluxed for 20 h, cooled to room temperature, and filtered through a 2-in. pad of alumina. The filtrate was evaporated under reduced pressure, and the product recrystallized from CH_3OH to yield 3.04 g (87%) of **37**: ^{1}H NMR ($CDCl_3$) δ 8.53 (d, 2 H, Ar), 7.64 (s, 4 H, Ar), 7.06 (d, 2 H, Ar), 2.56 (s, 6 H, CH_3).



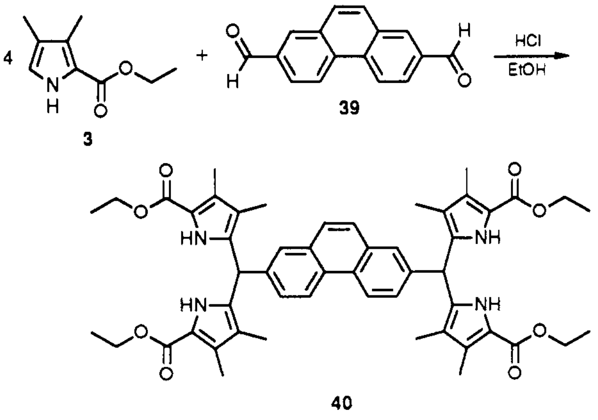
(29)

2,7-Bis(dibromomethyl)phenanthrene (38). **37** (2.00 g) was dissolved in 25 mL of CCl_4 in a 250-mL round-bottom flask. NBS (7.76 g) was mixed with 25 mL of CCl_4 and added to the aromatic solution. CCl_4 (25 mL) was used to complete the transfer. A few crystals of benzoyl peroxide were added, and the mixture was brought to a reflux for 20 h. The solution was filtered while hot, the solids were washed well with CH_2Cl_2, and then the solvent was removed under reduced pressure. The solids were dissolved in benzene and then precipitated with petroleum ether. The product was used without further purification, 3.16 g (62%).



(30)

2,7-Diformylphenanthrene (39). **38** (3.13 g) was dissolved in 50 mL of glacial HOAc. A solution of 2.00 g of NaOAc in 50 mL of glacial HOAc was added, and the mixture was brought to a reflux. H_2O (10 mL) was added, and the reaction was refluxed for 3 h under N_2. At the end of 3 h, 15 mL of glacial HOAc was added and the reaction was allowed to cool. After reaching room temperature, it was poured into 200 mL of H_2O and placed in the refrigerator overnight. The solid was filtered and dried, dissolved in CH_2Cl_2, and filtered through a 1-in. pad of alumina. The filtrate was collected, the solvent was removed under reduced pressure, and the product was crystallized from CH_2Cl_2/hexanes to yield 0.2426 g (17%) of **39**: ^{1}H NMR ($CDCl_3$) δ 10.21 (s, 2 H, COH), 8.82 (d, 2 H, Ar), 8.20 (s, 2 H, Ar), 8.17 (d, 2 H, Ar), 7.95 (s, 2 H, Ar).



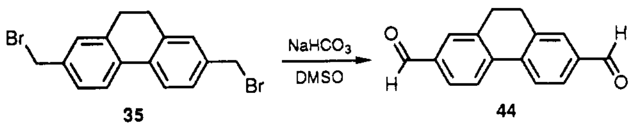
(31)

2,7-Bis[3,3′,4,4′-tetramethyl-5,5′-bis(ethoxycarbonyl)-2,2′-dipyrrylmethyl]phenanthrene (40). **39** (0.1502 g) and 0.4289 g of **3** were heated in 4.3 mL of absolute EtOH until both dissolved. The mixture was placed under N_2, and 0.10 mL of HCl was added. The mixture was refluxed for 1 h. The reaction was cooled to room temperature and then placed in the refrigerator overnight. The white solid was filtered, washed with 80% EtOH, and dried to yield 0.4873 g (88%) of **40**: ^{1}H NMR ($CDCl_3$) δ 8.56 (d, 2 H, Ar), 8.28 (br s, 4 H, NH), 7.62 (s, 2 H, Ar), 7.51 (d, 2 H, Ar), 7.37 (d, 2 H, Ar), 5.68 (s, 2 H, CH), 4.20 (q, 8 H, $C\mathit{H}_2CH_3$), 2.22 (s, 12 H, CH_3), 1.78 (s, 12 H, CH_3), 1.27 (t, 12 H, $CH_2C\mathit{H}_3$).

2,7-Bis(3,3′,4,4′-tetramethyl-5,5′-dicarboxy-2,2′-dipyrrylmethyl)phenanthrene (41). (See reaction 12.) **40** (0.4720 g) was suspended in 9.2 mL of absolute EtOH and brought to reflux. A 5 M NaOH solution (1.2 mL) was added, and the reaction mixture was refluxed for 18 h under N_2. The EtOH was removed under reduced pressure, and the residue was dissolved in H_2O and filtered. The filtrate was slowly acidified with 1 M HOAc. The precipitate was filtered, washed with H_2O, and dried in vacuo. The product was used without further purification, 0.3985 g (97%).

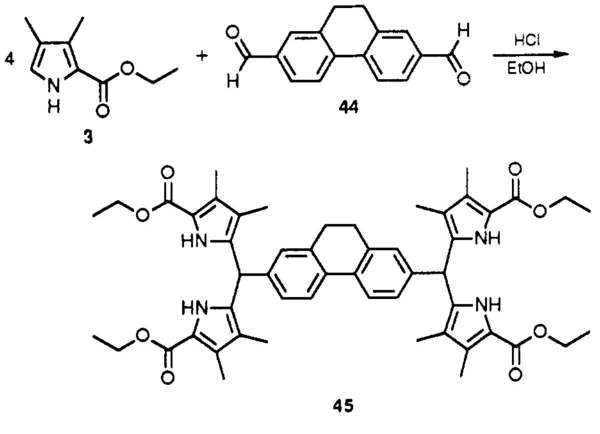
2,7-Bis(3,3′,4,4′-tetramethyl-2,2′-dipyrrylmethyl)phenanthrene (42). (See reaction 13.) **41** (0.3985 g) was dissolved in 5.4 mL of degassed ethanolamine. The solution was placed under N_2 and refluxed for 1 h, after which it was poured into 30 mL of ice H_2O while still warm. A gold solid soon separated, which was filtered, washed with H_2O, and dried in vacuo to yield 0.2191 g (71%) of **42**: ^{1}H NMR ($CDCl_3$) δ 8.53 (d, 2 H, Ar), 7.60 (s, 2 H, Ar), 7.56 (s, 2 H, Ar), 7.39 (d, 2 H, Ar), 7.29 (br s, 4 H, NH), 6.38 (s, 4 H, αH), 5.66 (s, 2 H, CH), 2.00 (s, 12 H, CH_3), 1.78 (s, 12 H, CH_3).

2,7-Bis(1,8-diethyl-2,3,4,5,6,7-hexamethylporphyrinyl)phenanthrene (43). (See reaction 14.) **42** (0.2035 g) was dissolved in 83.4 mL of dry CH_2Cl_2, and then 0.2014 g of **10** in 58.5 mL of dry CH_2Cl_2 was added. The reaction was carefully protected from light by wrapping the flask in aluminum foil. $TsOH{\cdot}H_2O$ (1.02 g) in 16.6 mL of dry MeOH was added and the reaction was stirred at room temperature for 6 h in air. Saturated $Zn(OAc)_2$ (16.6 mL) in dry CH_3OH was then added, and the reaction was stirred for 48 h. The reaction mixture was washed sequentially with H_2O, then with saturated $NaHCO_3$, and with H_2O again. The organic layer was then dried with Na_2SO_4, and the solvent was removed under reduced pressure. It was then chromatographed on silica (CH_2Cl_2), and the porphyrin bands were collected. The Zn was removed with trifluoroacetic acid (TFA). The mixture of porphyrins was then rechromatographed on silica (CH_2Cl_2/1% CH_3OH). The slow-moving bands were separated by preparative TLC on alumina plates to yield 0.0026 g (0.7%) of **43**: ^{1}H NMR ($CDCl_3$) δ 10.14 (s, 4 H, $\alpha + \gamma$ meso), 9.94 (s, 2 H, β meso), 9.00 (d, 2 H, Ar), 8.52 (s, 2 H, Ar), 8.36 (d, 2 H, Ar), 8.01 (s, 2 H, Ar), 4.06 (q, 8 H, $C\mathit{H}_2CH_3$), 3.62 (s, 12 H, CH_3), 3.46 (s, 12 H, CH_3), 2.32 (s, 12 H, CH_3), 1.84 (t, 12 H, $CH_2C\mathit{H}_3$), −3.14 (br s, 2 H, NH), −3.31 (br s, 2 H, NH); MS *m/e* 1076.6269 (1076.6270 calcd).



(32)

2,7-Diformyl-9,10-dihydrophenanthrene (44). **35** (3.5298 g) and 13.50 g of $NaHCO_3$ were placed in a 250-mL round-bottom flask, and 100 mL of DMSO was added. The reaction was heated to 115 °C under N_2 for 3.5 h. The reaction mixture was then allowed to cool to room temperature, after which it was poured into 150 mL of H_2O. The precipitate was filtered, dissolved in CH_2Cl_2, washed with H_2O, and dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude aldehyde was chromatographed on silica (CH_2Cl_2) to yield 0.8467 g (37%) of **44**: ^{1}H NMR ($CDCl_3$) δ 10.04 (s, 2 H, COH), 7.98 (d, 2 H, Ar), 7.86 (d, 2 H, Ar), 7.80 (s, 2 H, Ar), 3.01 (s, 4 H, CH_2).



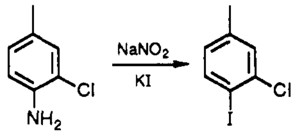
(33)

2,7-Bis[3,3′,4,4′-tetramethyl-5,5′-bis(ethoxycarbonyl)-2,2′-dipyrrylmethyl]-9,10-dihydrophenanthrene (45). **44** (0.2557 g) and 0.7249 g of **3** were heated in 7.3 mL of absolute EtOH until both dissolved. The reaction mixture was placed under N_2, and 0.17 mL of HCl was added. The mixture was refluxed for 1 h. Upon cooling the product crystallized. It was filtered, washed with cold EtOH, and dried to yield 0.8499 g (90%) of **45**: ^{1}H NMR ($CDCl_3$) δ 8.32 (br s, 4 H, NH), 7.61 (d, 2 H, Ar), 6.96 (d, 2 H, Ar), 6.91 (s, 2 H, Ar), 5.44 (s, 2 H, CH), 4.20 (q, 8 H, CH_2CH_3), 2.74 (s, 4 H, CH_2), 2.20 (s, 12 H, CH_3), 1.78 (s, 12 H, CH_3), 1.26 (t, 12 H, CH_2CH_3).

2,7-Bis(3,3′,4,4′-tetramethyl-5,5′-dicarboxy-2,2′-dipyrrylmethyl)-9,10-dihydrophenanthrene (46). (See reaction 12.) **45** (0.8307 g) was suspended in 10.3 mL of absolute EtOH and brought to reflux. A 5 M NaOH solution (1.3 mL) was added, and the reaction mixture was refluxed for 18 h under N_2. The EtOH was removed under reduced pressure, and the residue was dissolved in H_2O and filtered. The filtrate was slowly acidified with 1 M HOAc. The pink precipitate was filtered, washed with H_2O, dried in vacuo, and then used without further purification.

2,7-Bis(3,3′,4,4′-tetramethyl-2,2′-dipyrrylmethyl)-9,10-dihydrophenanthrene (47). (See reaction 13.) **46** (0.7689 g) was dissolved in 10.5 mL of degassed ethanolamine. The solution was placed under N_2 and refluxed for 1 h. The reaction mixture was poured into 50 mL of ice H_2O while still warm. A yellow-beige solid soon separated, which was filtered, washed with H_2O, and dried in vacuo to yield 0.5103 g (86%) of **47**: ^{1}H NMR ($CDCl_3$) δ 8.60 (d, 2 H, Ar), 7.29 (br s, 4 H, NH), 6.99 (d, 2 H, Ar), 6.97 (s, 2 H, Ar), 6.36 (s, 4 H, αH), 5.42 (s, 2 H, CH), 2.74 (s, 4 H, CH_2), 1.99 (s, 12 H, CH_3), 1.78 (s, 12 H, CH_3).

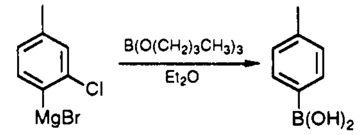
2,7-Bis(1,8-diethyl-2,3,4,5,6,7-hexamethylporphyrinyl)-9,10-dihydrophenanthrene (48). (See reaction 14.) **47** (0.2004 g) was dissolved in 82.8 mL of dry CH_2Cl_2, and then 0.1981 g of **10** in 57.25 mL of dry CH_2Cl_2 was added. The reaction was carefully protected from light by wrapping the flask in aluminum foil. $TsOH{\cdot}H_2O$ (1.00 g) in 16.1 mL of dry CH_3OH was added, and the reaction was stirred at room temperature for 6 h in air. Saturated $Zn(OAc)_2$ (16.1 mL) in dry CH_3OH was then added, and the reaction mixture was stirred for 60 h. The reaction mixture was washed sequentially with H_2O, then with saturated $NaHCO_3$, and with H_2O again. The organic layer was then dried with Na_2SO_4, and the solvent was removed under reduced pressure. It was then chromatographed on silica (CH_2Cl_2), and the porphyrin bands were collected. The Zn was removed with TFA, and the mixture of porphyrins was rechromatographed on silica (CH_2Cl_2/1% CH_3OH). The slow-moving bands were then chromatographed on alumina (CH_2Cl_2/hexanes, 1:1) to yield 0.0042 g (1%) of **48**: ^{1}H NMR ($CDCl_3$) δ 10.14 (s, 4 H, $\alpha + \gamma$ meso), 9.91 (s, 2 H, β meso), 8.08 (d, 2 H, Ar), 7.98 (d, 2 H, Ar), 7.86 (s, 2 H, Ar), 4.02 (q, 8 H, CH_2CH_3), 3.60 (s, 12 H, CH_3), 3.49 (s, 6 H, $12H_3$), 3.06 (s, 4 H, CH_2), 2.52 (s, 12 H, CH_3), 1.84 (t, 12 H, CH_2CH_3), −3.2 to −3.3 (br s, 4 H, NH); MS *m/e* 1078.6349 (1078.6349 calcd).



49

(34)

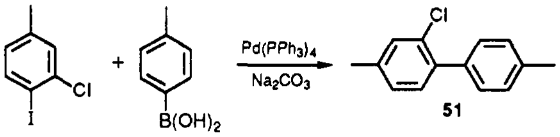
3-Chloro-4-iodotoluene (49). 4-Amino-3-chlorotoluene (25 g) was placed in a 400-mL beaker, and 82.8 mL of HCl was added followed by 55.2 g of ice. The mixture was cooled to 0 °C in an ice/salt bath with stirring. $NaNO_2$ (13.42 g) in 55.2 mL of H_2O was added slowly so as to maintain the reaction temperature between 0 and 5 °C. After the addition was complete, the reaction was stirred for 15 min and then filtered through a glass wool plug into a 1500-mL beaker containing 99.38 g of KI in 330 mL of H_2O. After standing overnight, the reaction was extracted with ether and washed sequentially with 10% NaOH, 5% $NaHSO_3$, and H_2O. It was then dried with Na_2SO_4, and the solvent was removed under reduced pressure to yield 38.67 g (86%) of **49** as a red oil: ^{1}H NMR ($CDCl_3$) δ 7.69 (d, 2 H, Ar), 7.28 (s, 1 H, Ar), 6.76 (d, 1 H, Ar), 2.28 (s, 3 H, CH_3).



50

(35)

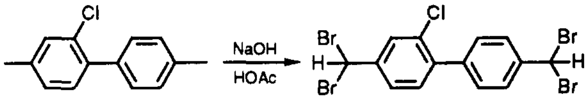
***p*-Tolylboronic Acid (50).** *n*-Butyl borate (58 g) in 100 mL of dry ether was placed in a 500-mL three-neck round-bottom flask equipped with a mechanical stirrer and cooled to −70 °C (CO_2/acetone bath). A solution of 1 M *p*-tolylmagnesium bromide (250 mL) in ether was added over a period of 1 h under N_2. The reaction was then allowed to warm slowly to 0 °C in the cooling bath. The mixture was slowly poured into 150 mL of cold 10% H_2SO_4 with stirring. The organic layer was separated, and the aqueous layer extracted twice with ether. The organic fractions were combined, and the ether was removed under reduced pressure. The butanol solution was made alkaline with a KOH solution, and H_2O was added until there was approximately 150 mL of H_2O beneath the organic layer. The butanol was removed as the H_2O azeotrope. The pH was adjusted to 4 with 10% H_2SO_4, and the mixture was diluted to 150 mL. The solution was heated to boiling and filtered hot. The product crystallized as white needles upon cooling to yield 22 g (65%) of **50**: ^{1}H NMR ($CDCl_3$) δ 7.62 (d, 2 H, Ar), 7.52 (d, 1 H, OH), 7.19 (d, 1 H, OH), 7.15 (d, 2 H, Ar), 2.34 (s, 3 H, CH_3).



49 **50** **51**

(36)

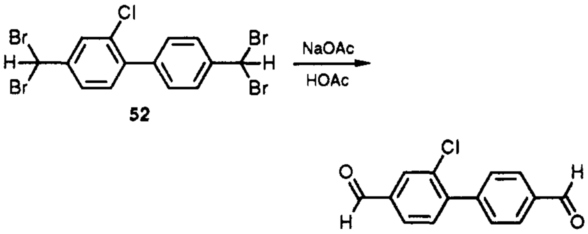
4,4′-Dimethyl-2-chloro-1,1′-biphenyl (51). **49** (10 g) and 80 mL of benzene were placed in a 250-mL round-bottom flask. $Pd(PPh_3)_4$ (1.39 g) was added followed by 40 mL of 2 M Na_2CO_3. **50** (5.93 g) in 20 mL of absolute EtOH was added, and the mixture was refluxed under N_2 with rapid stirring overnight. H_2O_2 (30%, 2 mL) was added after the reaction had cooled, and it was then stirred for 1 h. The reaction mixture was extracted with ether, washed with brine, and dried with Na_2SO_4, and the solvent was removed under reduced pressure. The oil was then purified by flask to flask distillation at reduced pressure to yield 6.72 g (78%) of **51** as a pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.42 (d, 2 H, Ar), 7.36 (s, 1 H, Ar), 7.29–7.32 (m, 3 H, Ar), 7.16 (d, 1 H, Ar), 2.48 (s, 3 H, CH_3), 2.42 (s, 3 H, CH_3).



51 **52**

(37)

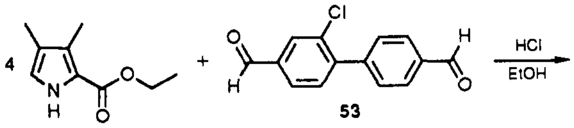
4,4′-Bis(dibromomethyl)-2-chloro-1,1′-biphenyl (52). **51** (5 g) and 200 mL of CCl_4 were placed in a 500-mL round-bottom flask. NBS (18.41 g) and a few crystals of benzoyl peroxide were added, and the reaction was refluxed for 20 h. The mixture was filtered hot, and the solids were washed with CCl_4. The solvent was removed, and the product was used without further purification.



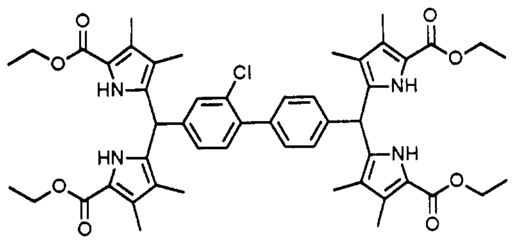
52 **53**

(38)

4,4′-Diformyl-2-chloro-1,1′-biphenyl (53). Crude **52** (11 g) was dissolved in 300 mL of HOAc containing 6 g of NaOH. The reaction was refluxed for 3 h under N_2 and then poured into 600 mL of H_2O. It was then extracted with CH_2Cl_2 and dried with Na_2SO_4, and the solvent was removed under reduced pressure. The resulting oil was dissolved in CH_3OH, and 0.5 g of K_2CO_3 was added. The mixture was stirred for 30 min, after which the solvent was removed and the crude dialdehyde chromatographed on silica (CH_2Cl_2) to yield 1.39 g (25%) of **53** as a white powder: ^{1}H NMR ($CDCl_3$) δ 10.09 (s, 1 H, COH), 10.03 (s, 1 H, COH), 8.01 (s, 1 H, Ar), 7.99 (d, 2 H, Ar), 7.86 (d, 1 H, Ar), 7.62 (d, 2 H, Ar), 7.53 (d, 1 H, Ar).



3 **53**



(39)

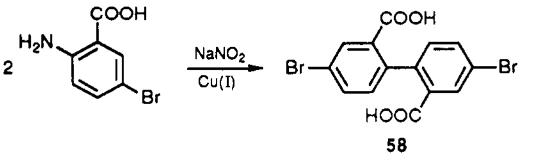
54

4,4′-Bis[3,3′,4,4′-tetramethyl-5,5′-bis(ethoxycarbonyl)-2,2′-dipyrrylmethyl]-2-chloro-1,1′-biphenyl (54). **53** (0.75 g) and 2.04 g of **3** were heated in 20.6 mL of absolute EtOH until both dissolved. The mixture was placed under N_2, and 0.49 mL of HCl was added. The mixture was refluxed for 1 h. The reaction was cooled to room temperature and the product precipitated as a white solid. The solid was filtered, washed with 70% EtOH, and dried to yield 2.42 g (90%) of **54**: ^1H NMR ($CDCl_3$) δ 8.48 (br s, 2 H, NH), 8.43 (br s, 2 H, NH), 7.41 (d, 2 H, Ar), 7.29 (d, 1 H, Ar), 7.19 (s, 1 H, Ar), 7.14 (d, 2 H, Ar), 7.03 (d, 1 H, Ar), 5.56 (s, 1 H, CH), 5.52 (s, 1 H, CH), 4.27 (m, 8 H, CH_2CH_3), 2.25 (s, 12 H, CH_3), 1.83 (s, 12 H, CH_3), 1.33 (m, 12 H, CH_2CH_3).

4,4′-Bis(3,3′,4,4′-tetramethyl-5,5′-dicarboxy-2,2′-dipyrrylmethyl)-2-chloro-1,1′-biphenyl (55). (See reaction 12.) **54** (2 g) was suspended in 27.5 mL of absolute EtOH and brought to reflux. A 5 M NaOH solution (3.39 mL) was added, and the reaction mixture was refluxed for 18 h under N_2. The EtOH was removed under reduced pressure, and the residue was dissolved in H_2O and then filtered. The filtrate was slowly acidified with 1 M HOAc. The precipitate was filtered, washed with H_2O, and dried in vacuo. The product was used without further purification, 1.42 g (81%).

4,4′-Bis(3,3′,4,4′-tetramethyl-2,2′-dipyrrylmethyl)-2-chloro-1,1′-biphenyl (56). (See reaction 13.) **55** (1.36 g) was dissolved in 23.4 mL of degassed ethanolamine. The solution was placed under N_2 and refluxed for 1 h, after which it was poured into 75 mL of ice H_2O while still warm. A gold solid soon separated, which was filtered, washed with H_2O, and dried in vacuo to yield 0.98 g (93%) of **56**: ^1H NMR ($CDCl_3$) δ 7.36 (m, 7 H, NH, Ar), 7.22 (s, 1 H, Ar), 7.18 (d, 2 H, Ar), 7.05 (d, 1 H, Ar), 6.40 (s, 4 H, αH), 5.52 (s, 1 H, CH), 5.49 (s, 1 H, CH), 2.02 (s, 12 H, CH_3), 1.83 (s, 12 H, CH_3).

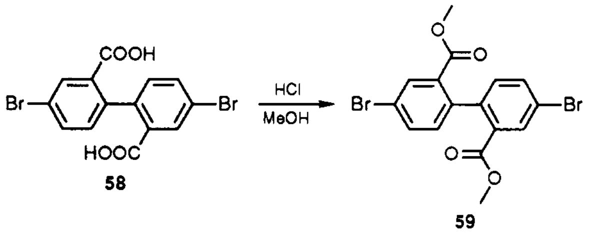
4,4′-Bis(1,8-diethyl-2,3,4,5,6,7-hexamethylporphyrinyl)-2-chloro-1,1′-biphenyl (57). (See reaction 14.) **56** (0.2081 g) was dissolved in 84.8 mL of dry CH_2Cl_2, and then 0.2030 g of **10** in 58.7 mL of dry CH_2Cl_2 was added. The reaction was carefully protected from light by wrapping the flask in aluminum foil. $TsOH{\cdot}H_2O$ (1.0247 g) in 16.5 mL of dry CH_3OH was added and the reaction stirred at room temperature for 6 h in air. Saturated $Zn(OAc)_2$ (16.5 mL) in dry CH_3OH was then added, and the reaction was stirred for 60 h. The reaction mixture was washed sequentially with H_2O, then with saturated $NaHCO_3$, and with H_2O again. The organic layer was then dried with Na_2SO_4, and the solvent was removed under reduced pressure. It was then chromatographed on silica (CH_2Cl_2), and the porphyrin bands were collected. The Zn was removed with TFA. The mixture of porphyrins was rechromatographed on silica (CH_2Cl_2/2% CH_3OH). The slow-moving bands were collected and chromatographed again on silica. The column was packed and eluted with EtOAc until all moving bands were off the column, and then CH_2Cl_2/2% CH_3OH was used to elute the dimer, yielding 0.0066 g (1.7%) of **57**: ^1H NMR ($CDCl_3$) δ 10.24 (sp s, 4 H, $\alpha + \gamma$ meso), 10.00 (sp s, 2 H, β meso), 8.39 (s, 1 H, Ar), 8.30 (d, 2 H, Ar), 8.17 (m, 3 H, Ar), 8.11 (d, 1 H, Ar), 4.10 (q, 8 H, CH_2CH_3), 3.68 (s, 12 H, CH_3), 3.61 (sp s, 12 H, CH_3), 2.76 (s, 6 H, CH_3), 2.72 (s, 6 H, CH_3), 1.91 (t, 12 H, CH_2CH_3), −3.14 (br s, 2 H, NH), −3.27 (br s, 2 H, NH); MS *m/e* 1086.5846 (1086.5803 calcd).



(40)

58

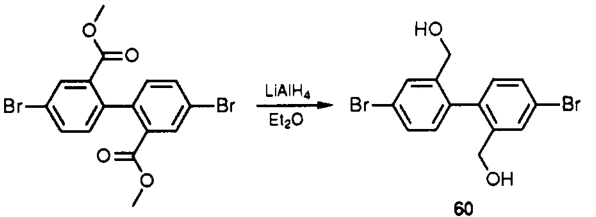
4,4′-Dibromo-2,2′-dicarboxy-1,1′-biphenyl (58). 2-Amino-5-bromobenzoic acid (19.71 g) was ground in a mortar with 37.5 mL of H_2O and 23 mL of HCl and was then transferred to a 250-mL round-bottom flask. The mixture was cooled to 0 °C in an ice/salt bath, and 6.58 g of $NaNO_2$ in 87.5 mL of H_2O was added dropwise over 30 min so as to maintain the reaction temperature below 5 °C. The mixture was filtered and kept at 5 °C while the Cu(I) solution was prepared. $CuSO_4{\cdot}5H_2O$ (31.5 g) was dissolved in 125 mL of H_2O in a 1-L beaker. NH_4OH (52.5 mL) was added and the solution was cooled to 10 °C. $NH_3OH{\cdot}HCl$ (8.90 g) in 30 mL of H_2O was mixed with 21.3 mL of 6 M NaOH, cooled to 10 °C, and added to the copper solution. The diazonium solution was added at a rate of 10 mL/min to the copper solution through a funnel dipped below the surface of the copper solution and then curved back upward to prevent gas evolution into the diazonium solution. The mixture was maintained at 10 °C for 5 min and then heated rapidly to boiling, at which point it was acidified with 62.5 mL of HCl. The reaction was cooled and then stood overnight. The solid was filtered, washed with H_2O, and then suspended in 50 mL of H_2O. $NaHCO_3$ (10 g) was carefully added, and the product was filtered, washed with H_2O, and dried to yield 17.32 g (47%) of **58**: ^1H NMR (D_2O (sodium salt)) δ 7.56 (s, 2 H, Ar), 7.44 (d, 2 H, Ar), 7.08 (d, 2 H, Ar).



58 **59**

(41)

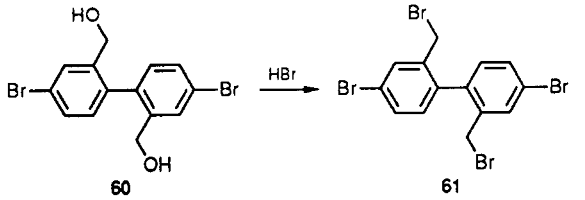
4,4′-Dibromo-2,2′-bis(methoxycarbonyl)-1,1′-biphenyl (59). **58** (17.32 g) was added to 50 mL of dry MeOH saturated with anhydrous HCl gas. The mixture was stirred at room temperature for 48 h, and the solvent was removed under reduced pressure. The solid was dissolved in 100 mL of CH_2Cl_2 and extracted with 50 mL of 1 M NaOH. The organic layer was separated and dried with Na_2SO_4, and the solvent was removed under reduced pressure. CH_3OH (75 mL) was added and the product crystallized. It was filtered and washed with cold CH_3OH to yield 9.01 g (49%) of **59**: ^1H NMR ($CDCl_3$) δ 8.12 (s, 2 H, Ar), 7.62 (d, 2 H, Ar), 7.00 (d, 2 H, Ar), 3.64 (s, 6 H, CH_3).



59 **60**

(42)

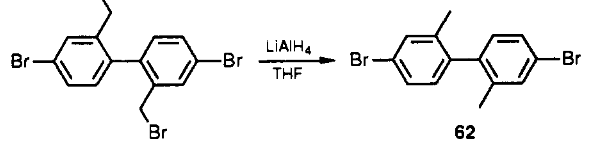
4,4′-Dibromo-2,2′-bis(hydroxymethyl)-1,1′-biphenyl (60). **59** (7.90 g) was dissolved in 100 mL of dry Et_2O, and 1.40 g of $LiAlH_4$ was cautiously added. The reaction was placed under N_2 and stirred at room temperature for 48 h. EtOAc (4 mL) was cautiously added followed by 10 mL of H_2O. The mixture was partitioned between 200 mL of 10% H_2SO_4 and Et_2O and then stirred at room temperature for 1 h. The aqueous phase was extracted with Et_2O, and the organic fractions were combined, washed with saturated $NaHCO_3$, and dried with Na_2SO_4. The Et_2O was removed under reduced pressure. The product was crystallized from EtOH to yield 6.16 g (90%) of **60**: ^1H NMR ($CDCl_3$) δ 7.63 (s, 2 H, Ar), 7.43 (d, 2 H, Ar), 6.96 (d, 2 H, Ar), 4.24 (s, 4 H, CH_2), 2.69 (s, 2 H, OH).



60 **61**

(43)

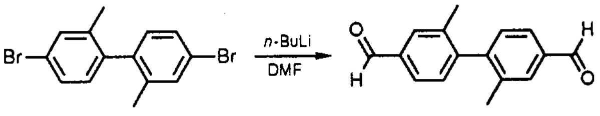
4,4′-Dibromo-2,2′-bis(bromomethyl)-1,1′-biphenyl (61). **60** (6.94 g) was dissolved in 20 mL of 33% HBr in HOAc. The reaction was placed under N_2 and heated to 80 °C for 18 h. The mixture was cooled to room temperature, and 40 mL of H_2O was added. The mixture was stirred for an additional 15 min, and then the solid was filtered and dried in vacuo to yield 7.40 g (79%) of **61**: ^1H NMR ($CDCl_3$) δ 7.64 (s, 2 H, Ar), 7.46 (d, 2 H, Ar), 7.08 (d, 2 H, Ar), 4.21 (d, 2 H, CH_2), 4.05 (d, 2 H, CH_2).



61 **62**

(44)

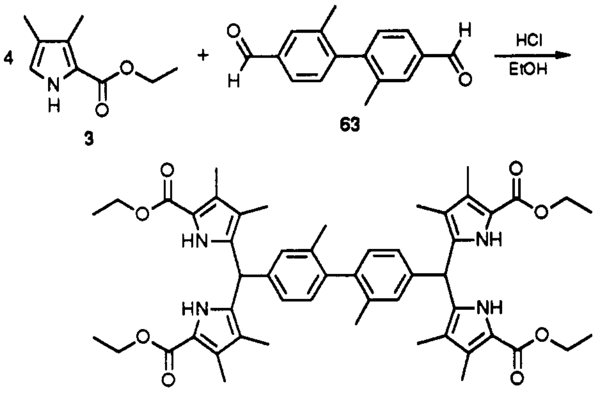
4,4'-Dibromo-2,2'-dimethyl-1,1'-biphenyl (62). 61 (7.10 g) was dissolved in 75 mL of dry THF, and 1.09 g of $LiAlH_4$ was added. The reaction was placed under N_2 and stirred at room temperature for 20 h. A concentrated solution of NaOH was then added dropwise until vigorous H_2 evolution ceased. $MgSO_4$ was added, and the reaction mixture was filtered. The solids were washed well with Et_2O, and the filtrate was evaporated to yield an oil which later solidified to yield 4.73 g (97%) of 62: ^1H NMR ($CDCl_3$) δ 7.40 (s, 2 H, Ar), 7.32 (d, 2 H, Ar), 6.90 (d, 2 H, Ar), 1.98 (s, 6 H, CH_3).



(45)

62 63

4,4'-Diformyl-2,2'-dimethyl-1,1'-biphenyl (63). 62 (4.93 g) was dissolved in 150 mL of petroleum ether and placed under N_2. A 1.55 M *n*-butyllithium solution (20.6 mL) in hexanes was added dropwise, and the solution was refluxed for 20 h. Dry, degassed DMF (3.47 mL) was added, and the reaction was refluxed for an additional 22 h. The solvents were removed under reduced pressure, and the solid residue was stirred with 50 mL of THF and 50 mL of 3 M HCl at room temperature for 45 min. The organic layer was separated, washed with saturated $NaHCO_3$ until alkaline, and dried with Na_2SO_4, and the solvent was removed under reduced pressure. The yellow-brown oil was chromatographed twice on silica ($MeCl_2$) to yield 1.04 g (30%) of 63 as a yellow oil: ^1H NMR ($CDCl_3$) δ 10.01 (s, 2 H, COH), 7.99 (s, 2 H, Ar), 7.94 (d, 2 H, Ar), 7.25 (d, 2 H, Ar), 2.10 (s, 6 H, CH_3).



3 63

(46)

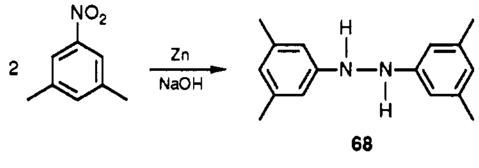
64

4,4'-Bis[3,3',4,4'-tetramethyl-5,5'-bis(ethoxycarbonyl)-2,2'-dipyrrylmethyl]-2,2'-dimethyl-1,1'-biphenyl (64). 63 (0.1275 g) and 0.3579 g of 3 were heated in 3.6 mL of absolute EtOH until both dissolved. The reaction mixture was placed under N_2, and 0.08 mL of HCl was added. The mixture was refluxed for 1 h. The solution was slowly cooled to room temperature and then placed in the refrigerator overnight. The product was filtered, washed with cold 70% EtOH, and dried to yield 0.45 g (96%) of 64: ^1H NMR ($CDCl_3$) δ 8.20 (br s, 4 H, NH), 7.04 (d, 2 H, Ar), 6.94 (s, 2 H, Ar), 6.88 (d, 2 H, Ar), 5.44 (s, 2 H, CH), 4.22 (q, 8 H, CH_2CH_3), 2.22 (s, 12 H, CH_3), 1.94 (s, 6 H, CH_3), 1.75 (s, 12 H, CH_3), 1.28 (t, 12 H, CH_2CH_3).

4,4'-Bis(3,3',4,4'-tetramethyl-5,5'-dicarboxy-2,2'-dipyrrylmethyl)-2,2'-dimethyl-1,1'-biphenyl (65). (See reaction 12.) 64 (0.3746 g) was suspended in 7.3 mL of absolute EtOH and brought to reflux. A 5 M NaOH solution (1.0 mL) was added, and the reaction was refluxed for 18 h under N_2. The EtOH was removed under reduced pressure, and the residue was dissolved in 25 mL of H_2O and filtered. The filtrate was slowly acidified with 1 M HOAc. The pink precipitate was filtered, washed with H_2O, dried in vacuo, and then used without further purification, 0.3198 g (98%).

4,4'-Bis(3,3',4,4'-tetramethyl-2,2'-dipyrrylmethyl)-2,2'-dimethyl-1,1'-biphenyl (66). (See reaction 13.) 65 (0.3198 g) was dissolved in 4.4 mL of degassed ethanolamine. The solution was placed under N_2 and refluxed for 1 h, after which the reaction mixture was poured into 30 mL of ice H_2O while still hot. A gold solid soon separated, which was filtered, washed with H_2O, and dried in vacuo to yield 0.1745 g (71%) of 66: ^1H NMR ($CDCl_3$) δ 7.31 (br s, 4 H, NH), 7.00 (s, 2 H, Ar), 6.97 (d, 2 H, Ar), 6.89 (d, 2 H, Ar), 6.36 (s, 4 H, αH), 5.42 (s, 2 H, CH), 2.00 (s, 12 H, CH_3), 1.93 (s, 6 H, CH_3), 1.78 (s, 12 H, CH_3).

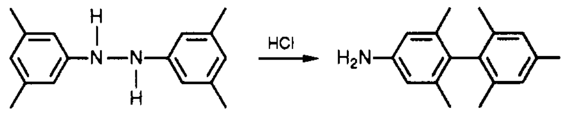
4,4'-Bis(1,8-diethyl-2,3,4,5,6,7-hexamethylporphyrinyl)-2,2'-dimethyl-1,1'-biphenyl (67). (See reaction 14.) 66 (0.1739 g) was dissolved in 70.8 mL of dry CH_2Cl_2, and then 0.1709 g of 10 in 49.6 mL of dry CH_2Cl_2 was added. The reaction was carefully protected from light by wrapping the flask in aluminum foil. $TsOH{\cdot}H_2O$ (0.87 g) in 14 mL of dry CH_3OH was added, and the reaction was stirred at room temperature for 6 h in air. Saturated $Zn(OAc)_2$ (14 mL) in dry CH_3OH was added, and the reaction was stirred for 72 h. The reaction mixture was washed sequentially with H_2O, then with saturated $NaHCO_3$, and with H_2O again. The organic layer was then dried with Na_2SO_4, and the solvent was removed under reduced pressure. It was then chromatographed on silica (CH_2Cl_2), and the fastest moving porphyrin bands were collected. The Zn was removed with TFA, and the mixture of porphyrins was rechromatographed on silica (CH_2Cl_2/1% CH_3OH) to yield 0.0041 g (1.3%) of 67: ^1H NMR ($CDCl_3$) δ 10.17 (s, 4 H, $\alpha + \gamma$ meso), 9.94 (s, 2 H, β meso), 8.10 (s, 2 H, Ar), 8.08 (d, 2 H, Ar), 7.82 (d, 2 H, Ar), 4.08 (q, 8 H, CH_2CH_3), 3.63 (s, 12 H, CH_3), 3.56 (s, 12 H, CH_3), 2.71 (s, 6 H, CH_3), 2.68 (s, 6 H, CH_3), 2.60 (s, 6 H, CH_3), 1.86 (t, 12 H, CH_2CH_3), −3.13 (br s, 2 H, NH), −3.86 (br s, 2 H, NH); MS *m/e* 1080.6437 (1080.6438 calcd).



(47)

68

1,2-Bis(3,5-dimethylphenyl)hydrazine (68). 3,5-Dimethylnitrobenzene (9.98 g), 25 g of Zn dust, and 40 mL of absolute EtOH were placed under N_2 in a 250-mL round-bottom flask. The mixture was heated to reflux, at which time heating was discontinued. NaOH (15 g) in 50 mL of H_2O was then added dropwise. The reaction boiled vigorously during the first half of the addition, after which external heating was necessary to maintain reflux. After the addition was complete, the reaction mixture was refluxed for 4 h under N_2 and then filtered while hot through a preheated Büchner funnel into 150 mL of 30% HOAc and 0.5 M $Na_2S_2O_5$. The filtered off sludge was extracted twice with 20 mL of boiling EtOH, and the extracts were added to the HOAc solution. The HOAc solution was cooled to 10 °C and a solid precipitated. The solid was filtered, washed with H_2O, and then dissolved in 85 mL of petroleum ether. The petroleum ether was heated to boiling and then decanted from the remaining H_2O. The solution was reheated to dissolve any precipitate and then allowed to cool to yield 5.52 g (35%) of 68 as glistening needles: ^1H NMR ($CDCl_3$) δ 6.46 (s, 6 H, Ar), 5.42 (s, 2 H, NH), 2.20 (s, 12 H, CH_3).

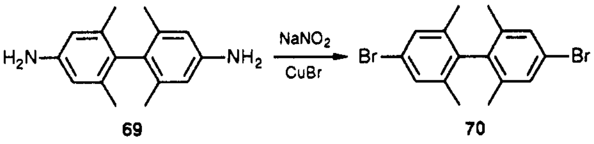


(48)

68

69

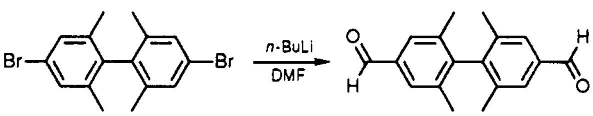
2,2',6,6'-Tetramethylbenzidine (69). HCl (10%, 260 mL) was degassed by bubbling N_2 through the solution for 30 min and then was heated to reflux. 68 (5.52 g) was added, and the reaction mixture was refluxed for 5 h under N_2, after which it was allowed to stand overnight. The solution was filtered, and the filtrate was boiled for 30 min with Norite. The charcoal was filtered off and the filtrate made alkaline by the addition of 20% NaOH until the solution became cloudy. A saturated NaOAc solution was then added to complete the basification. The solution was extracted with Et_2O (3 × 100 mL), dried with Na_2SO_4, and filtered, and the Et_2O was removed under reduced pressure. The solid was dissolved in 20 mL of hot benzene, and 40 mL of hexanes was added. The product precipitated to yield 3.55 g (64%) of 69: ^1H NMR ($CDCl_3$) δ 6.47 (s, 4 H, Ar), 3.58 (br s, 4 H, NH), 1.79 (s, 12 H, CH_3).



(49)

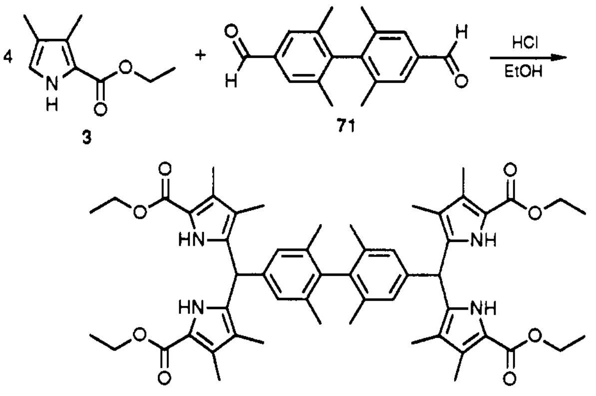
69 70

4,4'-Dibromo-2,2',6,6'-tetramethyl-1,1'-biphenyl (70). 69 (3.42 g) was dissolved in 31.4 mL of 10% H_2SO_4 in a 300-mL beaker and cooled to 10 °C in an ice bath. $NaNO_2$ (2.14 g) in 20 mL of H_2O was slowly added dropwise so as to maintain the temperature at 10 °C. The solution was stirred for 30 min at 10 °C and then poured into a cold solution of 21.38 g of CuBr in 214 mL of 48% HBr in a 1-L beaker. The reaction was slowly heated to 50 °C and stirred for 3 h, after which it was cooled to room temperature. The solution was extracted with Et_2O (3 × 50 mL), the Et_2O fractions were washed with 3 M HCl followed by H_2O and then dried with Na_2SO_4, and the solvent was removed under reduced pressure. The product was purified on alumina (petroleum ether) to yield 2.23 g (43%) of **70**: ^1H NMR (CD_2Cl_2) δ 7.28 (s, 4 H, Ar), 1.82 (s, 12 H, CH_3).



70 71 (50)

4,4′-Diformyl-2,2′,6,6′-tetramethyl-1,1′-biphenyl (71). **70** (2.1173 g) was suspended in 60 mL of petroleum ether and placed under N_2. A 1.55 M *n*-butyllithium solution (8.17 mL) in hexanes was cautiously added, and the reaction was refluxed for 20 h. Dried, degassed DMF (1.38 mL) was added, and the mixture was refluxed for 20 h under N_2. The solvents were removed under reduced pressure, and the residue was dissolved in a mixture of 50 mL of THF and 50 mL of 3 M HCl. The reaction was stirred for 45 min at room temperature and the organic layer separated. The aqueous layer was washed with Et_2O, and the organic fractions were combined. The solution was washed with $NaHCO_3$ until alkaline and then dried, and the solvent was removed under reduced pressure. The product was chromatographed on silica (CH_2Cl_2) and crystallized from CH_2Cl_2/hexanes to yield 0.4367 g (28%) of **71**: ^1H NMR ($CDCl_3$) δ 9.96 (s, 2 H, COH), 7.64 (s, 4 H, Ar), 1.93 (s, 12 H, CH_3).



3 71 72 (51)

4,4′-Bis[3,3′,4,4′-tetramethyl-5,5′-bis(ethoxycarbonyl)-2,2′-dipyrrylmethyl]-2,2′,6,6′-tetramethyl-1,1′-biphenyl (72). **71** (0.1789 g) and 0.4492 g of **3** were heated in 4.5 mL of absolute EtOH until both dissolved. The reaction mixture was placed under N_2, and 0.11 mL of HCl was added. The mixture was refluxed for 1 h. The solution was slowly cooled to room temperature and then placed in the refrigerator overnight. The product was filtered, washed with cold 80% EtOH, and dried to yield 0.5053 g (84%) of **72**: ^1H NMR ($CDCl_3$) δ 8.18 (br s, 4 H, NH), 6.80 (s, 4 H, Ar), 5.40 (s, 2 H, CH), 4.22 (q, 8 H, CH_2CH_3), 2.22 (s, 12 H, CH_3), 1.81 (s, 12 H, CH_3), 1.76 (s, 12 H, CH_3), 1.25 (t, 12 H, CH_2CH_3).

4,4′-Bis(3,3′,4,4′-tetramethyl-5,5′-dicarboxy-2,2′-dipyrrylmethyl)-2,2′,6,6′-tetramethyl-1,1′-biphenyl (73). (See reaction 12.) **72** (0.4131 g) was suspended in 5.7 mL of absolute EtOH and brought to reflux. A 5 M NaOH solution (0.70 mL) was added, and the reaction was refluxed under N_2 for 18 h. The EtOH was removed under reduced pressure, and the residue was dissolved in 30 mL of H_2O and filtered. The filtrate was slowly acidified with 1 M HOAc. The pink precipitate was filtered, washed with H_2O, dried in vacuo, and used without further purification, 0.3367 g (93%).

4,4′-Bis(3,3′,4,4′-tetramethyl-2,2′-dipyrrylmethyl)-2,2′,6,6′-tetramethyl-1,1′-biphenyl (74). (See reaction 13.) **73** (0.3367 g) was dissolved in 5.1 mL of degassed ethanolamine. The solution was placed under N_2 and refluxed for 1 h, after which the reaction mixture was poured into 55 mL of ice H_2O while still hot. A tan solid soon separated, which was filtered, washed with H_2O, and dried in vacuo to yield 0.2365 g (90%) of **74**: ^1H NMR ($CDCl_3$) δ 7.33 (br s, 4 H, NH), 6.86 (s, 4 H, Ar), 6.36 (s, 4 H, αH), 5.37 (s, 2 H, CH), 2.00 (s, 12 H, CH_3), 1.76 (split s, 24 H, CH_3).

4,4′-Bis(1,8-diethyl-2,3,4,5,6,7-hexamethylporphyrinyl)-2,2′,6,6′-tetramethyl-1,1′-biphenyl (75). (See reaction 14.) **74** (0.1776 g) was dissolved in 69.0 mL of dry CH_2Cl_2, and then 0.1666 g of **10** in 48.4 mL of dry CH_2Cl_2 was added. The reaction was carefully protected from light by wrapping the flask in aluminum foil. $TsOH{\cdot}H_2O$ (0.85 g) in 13.6 mL of dry CH_3OH was added, and the reaction was stirred at room temperature for 6 h in air. Saturated $Zn(OAc)_2$ (13.6 mL) in dry CH_3OH was added, and the reaction was stirred for 46 h. The reaction mixture was washed sequentially with H_2O, then with saturated $NaHCO_3$, and with H_2O again. The organic layer was then dried with Na_2SO_4, and the solvent was removed under reduced pressure. It was then chromatographed on silica (CH_2Cl_2), and the porphyrin bands were collected. The Zn was removed with TFA, and the mixture of porphyrins was rechromatographed on silica (CH_2Cl_2/1% CH_3OH). The product was separated by preparative TLC on alumina plates (80% CH_2Cl_2, 20% cyclohexane) to yield 0.0019 g (0.6%) of **75**: ^1H NMR ($CDCl_3$) δ 10.14 (s, 4 H, $\alpha + \gamma$ meso), 10.04 (s, 2 H, β meso), 7.84 (s, 4 H, Ar), 4.08 (q, 8 H, CH_2CH_3), 3.62 (s, 12 H, CH_3), 3.53 (s, 12 H, CH_3), 2.60 (s, 12 H, CH_3), 2.12 (s, 12 H, CH_3), 1.85 (t, 12 H, CH_2CH_3), −3.18 (br s, 2 H, NH), −3.85 (br s, 2 H, NH); MS *m/e* 1138.8445 (1138.8444 calcd).

Metalations. The mixed metal dimers were prepared by first inserting 1 equiv of Fe followed by an excess of Zn. The Fe insertion must be very carefully controlled to exclude Cu impurities. To this end, all solvents were distilled to remove trace Cu, and the reaction glassware was soaked in Cu-free HOAc before use. The metalation of the biphenyl dimer will serve to illustrate a typical reaction: 1.5 mg of the free base biphenyl dimer was dissolved in 0.10 mL of Cu-free pyridine, after which 2.0 mL of Cu-free glacial HOAc was added. $FeSO_4{\cdot}7H_2O$ (0.4 mg) was added, the solution was placed under N_2, and the flask was warmed in a preheated bath at 80 °C for 10 min. The solution was then allowed to cool in air before being poured into a separatory funnel containing 20 mL of Cu-free Et_2O and 20 mL of doubly distilled H_2O. The Et_2O layer was separated, washed with H_2O, and dried with Na_2SO_4. The solvent was removed under reduced pressure, and the product was chromatographed twice on neutral alumina with $CH_2Cl_2 \rightarrow CH_2Cl_2$/1% CH_3OH to yield 0.5 g. During the chromatography, any Cu-contaminated dimer eluted first followed by unmetalated dimer. After these bands were off the column, 1% CH_3OH was added and the Fe dimer then moved off the column as the μ-oxo dimer. The Fe dimer was dissolved in CH_2Cl_2, and a saturated solution of $Zn(OAc)_2$ in CH_3OH was then added. The reaction mixture was allowed to stand for 30 min, after which it was shaken with H_2O and dried with Na_2SO_4, and the solvent was removed under reduced pressure. The reaction mixture was then chromatographed on neutral alumina with CH_2Cl_2/1% CH_3OH. The bis-Fe dimer eluted first, followed by the mixed metal dimer. The dimers were stored dry, protected from light, as the μ-oxo Fe species until the transient absorbance measurements were ready to be made. Directly before these experiments, the μ-oxo dimers were broken up with 5% HOAc, after which imidazole was added to the dimer dissolved in DMF to yield the bis-imidazole, low-spin Fe(III) complex. For the static fluorescence measurements, the μ-oxo dimers were broken up, the compounds were dissolved in CH_2Cl_2, and imidazole was again added to obtain the low-spin Fe(III) complex.

Photophysical Measurements. Static emission spectra were obtained on a Perkin-Elmer MPF 44A spectrometer, using a total porphyrin absorbance <0.05 absorbance units, so that inner filter effects were negligible. Picosecond pump–probe measurements were made on a "homebuilt" YLF regenerative amplifier system, operating at 500 Hz, with a peak energy of ca. 10 μJ. (The excitation beam was split to generate a continuum for the probe beam.) This system is described in detail elsewhere. Finally, fluorescence lifetime measurements, which gave the most accurate rate constants, were made using a single photon counting instrument previously described.[8]

Acknowledgment. This work was supported by the NSF and, in part, the NIH (GM33881). We acknowledge the continued encouragement of Gerhard Closs in these investigations; this paper is dedicated to his memory.