intensity of mass 51 ion at a high C_2H_4/CH_3OH ratio suggests that ethylene molecules have the greater opportunity to react with the protonated methanol ion in the presence of trace methanol. Thereafter the solvating ethylene molecules form the observed $(C_2H_4)_n(CH_3OH)H_3O^+$ ions. This sequence of peaks is observed throughout the entire cluster mass spectrum to the limit of our sensitivity.

Acknowledgment. This work was carried out with financial assistance from the Korea Standards Research Institute and the Korea Science & Engineering Foundation, which is gratefully acknowledged. K.-H.J. owes particular thanks to Professor Alan L. Mackay, Birkbeck College, University of London, for reading the manuscript and for helpful discussions.

Registry No. Ethylene, 74-85-1; methanol, 67-56-1.

Push-Pull Porphyrins as Nonlinear Optical Materials

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Due to their potential applications for optical communications, data storage, and electrooptical signal processing, molecules with nonlinear optical (NLO) properties have been extensively investigated.[1] As part of our interest in porphyrins and metalloporphyrins as photoresponsive[2] and field-responsive materials,[3] we have synthesized a series of "push-pull" porphyrins containing both donor and acceptor substituents and have examined their NLO properties. The enhancements in molecular hyperpolarizabilities in previous organic systems have relied on donor–acceptor interactions along one-dimensional pathways; our porphyrinic compounds are prototypes of donor–acceptor interactions in two dimensions.

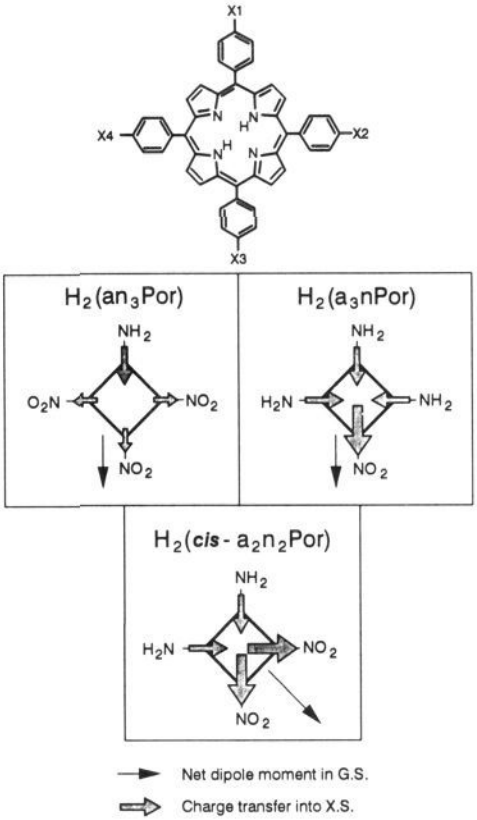

Figure 1. Structure, net dipole moment vectors, and charge-transfer transition vectors of push-pull porphyrins: $H_2(n_4Por)$, X1 = X2 = X3 = X4 = NO_2; $H_2(an_3Por)$, X1 = X2 = X3 = NO_2, X4 = NH_2; H_2(*trans*-a_2n_2Por), X1 = X3 = NO_2, X2 = X4 = NH_2; H_2(*cis*-a_2n_2Por), X1 = X2 = NO_2, X3 = X4 = NH_2; $H_2(a_3nPor)$, X1 = NO_2, X2 = X3 = X4 = NH_2; $H_2(a_4Por)$, X1 = X2 = X3 = X4 = NH_2; H_2TPP, X1 = X2 = X3 = X4 = H.

Porphyrins with their large π-conjugated system provide a versatile synthetic base to create effective intramolecular charge transfer (CT). As shown in Figure 1, the difunctionalized tetraarylporphyrins with nitro groups (n) as electron acceptors and amino groups (a) as electron donors have been prepared. The synthesis of $H_2(an_3Por)$, H_2(*cis*-a_2n_2Por), and $H_2(a_3nPor)$ does not involve the traditional crossed-condensation for multisubstituted porphyrins,[4] which are usually isolated only in low yields (<5%). Instead, $H_2(n_4Po4)$, $H_2(an_3Por)$, H_2(*trans*-a_2n_2Por), H_2(*cis*-a_2n_2Por), $H_2(a_3nPor)$, and $H_2(a_4Por)$ were prepared by the partial reduction of the nitro groups of 5,10,15,20-tetrakis(*p*-nitrophenyl)porphyrin[5] with 2.5 times the stoichiometric amount of $SnCl_2$. The reaction was performed under nitrogen in concentrated hydrochloric acid at 75 °C for 24 h. After the reaction was neutralized with concentrated ammonium hydroxide, the isolated solid mixture was placed in a Soxhlet apparatus and extracted with chloroform for 7 days. $H_2(an_3Por)$, H_2(*cis*-a_2n_2Por), and $H_2(a_3nPor)$ were separated from each other by column chromatography in ~30% isolated yields each. They have been fully characterized by elemental analysis, TLC, and FAB-MS, UV–visible, FTIR, and ^1H NMR spectroscopies, as provided in the supplementary material. The optical spectra of these porphyrins are included in the supplementary material and show no absorbances at wavelengths greater than 680 nm.

The structural control of β, the second-order molecular hyperpolarizability, is well understood from both theoretical and experimental perspectives.[6] Organic molecules with strong electron donor and electron acceptor groups that are connected by a large conjugated π-electron system usually show high β values. Following this general rule, a variety of stilbenes, polyenes, and diazo molecules have been designed that have β values up

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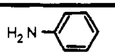
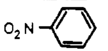
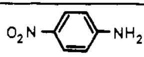
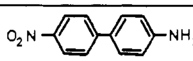
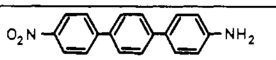
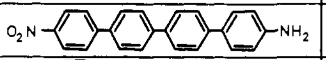
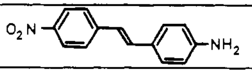
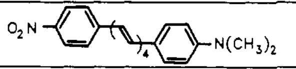
Table I. Dipole Moments and EFISH Hyperpolarizabilities of Various Nitro/Amino Disubstituted Arenes and Tetraphenylporphyrins[e]

Compound	μ (10^{-18} esu)[a]	β (10^{-30} esu)[a]
I 	1.5[b]	0.55[b]
II 	4.0[b]	1.9[b]
III 	6.2[c] 7.8[d]	9.2[c] 10[d]
IV 	5.0 7.8[d]	24 24[d]
V 	7.6[d]	16[d]
VI 	10[d]	11[d]
VII 	5.1	40
VIII 	9	190 ± 50
H_2(an$_3$Por)		≤10
H_2(*cis*-a$_2$n$_2$Por)	7±1	30±10
H_2(a$_3$nPor)	5±1	20±10

[a] In $CHCl_3$. [b] Neat. [c] In acetone. [d] In NMP. [e] The probe wavelength was 1.91 μm, derived from H_2 Raman shifting of a 10 ns pulsed Nd:YAG laser (1.06 μm), as described in ref 14. Data for compounds I–VIII from ref 9.

to 1000 × 10^{-30} esu.[7] Phthalocyanines, which have a similar π-conjugated macrocyclic ring, have been predicted *theoretically* to have relatively large β values (165 × 10^{-30} esu) after they are unsymmetrically difunctionalized with four nitro groups and four amino groups.[8]

Table I compares the electric-field-induced second-harmonic generation (EFISH) measurements of our porphyrins (in $CHCl_3$ at 1.91 μm) with their two-dimensional conjugation to other linear, high β molecules.[9] The three porphyrins show moderately high β values. They are significantly smaller, however, then that of the tetraene VIII. The β value determined by the EFISH technique is a polarizability projection from the full β tensor: it is the vector component projected onto the molecular dipole. The β value is therefore expected to be diminished when the two directions differ significantly. Thus, in EFISH measurements, linear π-conjugated molecules have the advantage compared to those with nonlinear, but similar sized, π systems. The additional dimensionality of the π-conjugated system in a direction perpendicular to the principal molecular axis actually reduces the overall NLO response.[10] This explains the unexpected smaller β values being found for dinitrosostilbenes compared to nitrostilbenes.[11]

A similar view can also be applied to H_2(an$_3$Por), H_2(*cis*-a$_2$n$_2$Por), and H_2(a$_3$nPor). As shown in Figure 1, the net dipole moment of H_2(an$_3$Por) and H_2(a$_3$nPor) is expected to be along the obvious mixed-substitution axis, while the moment of H_2(*cis*-a$_2$n$_2$Por) is expected along the axis of the pyrrole N atoms, bisecting the pyrrole rings. The influence of off-moment substituents is clearly reduced or canceled in this situation by geometric factors. The behavior of β is somewhat different. Despite the similarity between the dipole moments of their ground states, H_2(an$_3$Por) and H_2(a$_3$nPor) are not equivalent in the charge-transfer behavior of their excited states. Donating NH_2 groups push substantially less charge into the conjugation system than the accepting NO_2 groups withdraw in the excited CT states. In H_2(a$_3$nPor), charge is pushed into the total conjugation system by three donors and, in the excited CT state, pulled by one strong acceptor (shown schematically in Figure 1). The CT displacements are well aligned with the dipole axis and give a strong EFISH β value (20 × 10^{-30} esu). On the other hand, in H_2(an$_3$Por), only one donor pushes charge into the macrocycle, while this charge is drained by three competing strong acceptors. In the competing CT displacements, only one of the acceptor's contributions is well aligned with μ. Thus, H_2(an$_3$Por) displays a weaker EFISH β value (≤10 × 10^{-30} esu). This line of reasoning also explains the larger β value of H_2(*cis*-a$_2$n$_2$Por) (30 × 10^{-30} esu).

It is important in considering the potential of push-pull porphyrins to note that tetraarylporphyrins have a less effective intramolecular CT due to the dihedral twist between phenyl rings and the plane of the porphyrin. Because of steric hindrance, the phenyl ring is expected to be out of the plane of porphyrin. The X-ray crystallographic structure[12] of H_2TPP has an average dihedral angle of 60°. The rotational barriers of the phenyl rings have been determined by NMR techniques[13] and are found to be relatively high, ranging from 11 to 17 kcal/mol. Theoretical calculations have shown that the β value will be reduced by about 50% due to this torsional angle.[10] This dihedral angle effect in polyphenyl systems is apparent from the decreasing β values[14] for IV, V, and VI in Table I. NMR studies indicate that the effects of phenyl substituents on tetraarylporphyrins are transmitted to the porphyrin π system by a combination of σ and π induction, rather than σ induction and π conjugation.[15] A similar conclusion can be drawn from the NMR data on these porphyrins.[16] Further evidence of inefficient CT in H_2(an$_3$Por), H_2(*cis*-a$_2$n$_2$Por), and H_2(a$_3$nPor) can be found in their UV–visible spectra. The typical intramolecular CT absorption band occurs within the visible light region and depends on the size of π system. Its intensity can be comparable to that of the π–π* transitions of porphyrins, albeit broader.[17] The UV–visible spectra of these porphyrins, however, are dominated by the porphyrinic π–π* absorption bands and are similar in all six porphyrins (i.e., H_2(n$_4$Por), H_2(an$_3$Por), H_2(*trans*-a$_2$n$_2$Por), H_2(*cis*-a$_2$n$_2$Por), H_2(a$_3$nPor), and H_2(a$_4$Por)). Since a CT band is relatively weak, we must conclude that the coupling of the donor and acceptor groups across the porphyrin ring is limited.

In conclusion, we have synthesized and isolated the first set of porphyrins with tailored quadratic NLO properties and have measured them by the EFISH technique. Though the molecular hyperpolarizabilities of these porphyrins are substantial, they are lower than one might expect for such large conjugation systems. Two factors reduce the efficacy of CT enhancement of EFISH β values in these compounds. First, EFISH is primarily sensitive to CT parallel to the permanent dipole moment, but here substantial CT in perpendicular directions competes. Second, the intramolecular CT transitions are relatively weak in tetraarylporphyrins due to the dihedral angle between phenyl groups and

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the porphyrin ring. We are currently examining amphiphilic derivatives of these porphyrins as Langmuir–Blodgett films and the macroscopic NLO properties of these assemblies.

Acknowledgment. This work was supported by the National Institutes of Health and by the Department of Energy (EDFG02-91ER45439) with a research assistantship (C.T.C.).

Supplementary Material Available: Spectroscopic and analytical data for $H_3(an_3Por)$, H_2(*trans*-a_2n_2Por), H_2(*cis*-a_2n_2Por), and $H_2(a_3nPor)$ (4 pages). Ordering information is given on any current masthead page.

Rapid Detection of ^{57}Fe NMR Chemical Shifts of Model Hemes: An Approximate Correlation between ^{57}Fe and ^{31}P Chemical Shifts of Fe(II) Porphyrins Bound to Phosphine Axial Ligands

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The NMR chemical shift range of the ^{57}Fe nucleus is at least 12 000 ppm.[1-4] Therefore, ^{57}Fe NMR spectroscopy is potentially an extremely sensitive, direct probe of the electron density and asymmetry at the heme iron. However, the combination of low natural abundance (2.19%) and a low magnetogyric ratio makes the ^{57}Fe nucleus in natural abundance only 7.4×10^{-7} times as sensitive as the proton. Direct detection of ^{57}Fe resonances of model hemes and heme proteins[4-9] has therefore utilized isotopic enrichment of ^{57}Fe. Nevertheless, the direct detection of ^{57}Fe signals typically requires hours of NMR time and large volumes of enriched sample. Thus, indirect detection of ^{57}Fe rsonance frequencies is an attractive alternative method. La Mar and co-workers[10] showed some time ago that such double resonance techniques could allow the determination of ^{57}Fe chemical shifts of carbon monoxy complexes of heme proteins using ^{13}CO- and ^{57}Fe-enriches samples. Morishima[11] and Nozawa[12] have similarly determined ^{57}Fe chemical shifts using ^{15}N-enriched porphyrins. Koridze and co-workers[13] have utilized similar techniques, with ^{13}C as the observed nucleus, for ^{57}Fe-enriched ferrocenes and ferrocenyl cations, without ^{13}C enrichment. Benn and co-workers have utilized both ^{13}C[14] and ^{31}P[2,3] as the observed nucleus for investigating a number of ferrocenes[14] and phosphine-coordinated organometallic complexes of a number of low-γ metal nuclei.[2,3] The latter authors have also demonstrated the increased enhancement obtained by inverse 2D polarization transfer techniques.[2,3]

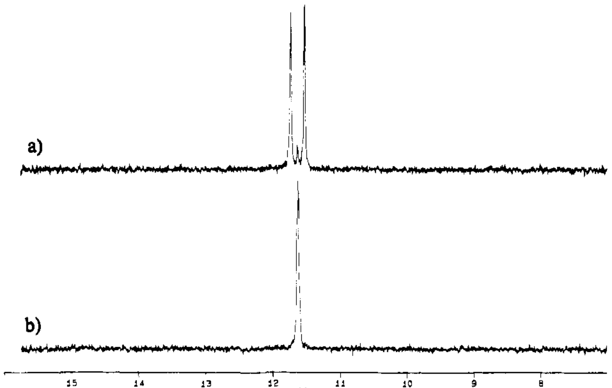

Figure 1. ^{31}P spectra of 95% ^{57}Fe-enriched $[(p\text{-}OCH_3)_4TPPFe(PMe_3)_2]$ at 25 °C in C_6D_6 (12 mM), recorded on a Bruker AM-500 spectrometer in the presence of broad band proton decoupling:[25] (a) off-resonance ^{57}Fe irradiation (128 acquisitions); (b) on-resonance ^{57}Fe irradiation, resulting in decoupling of the ^{31}P–^{57}Fe doublet (64 acquisitions). Chemical shifts are vs external 85% H_3PO_4; sample concentration was ~6 mM. Stepping through the ^{57}Fe frequency range around 16.2 MHz with a decoupling power of 0.5 W (bandwidth ~100 Hz) causes the ^{31}P doublet (J_{Fe-P} = 35–59 Hz) to collapse when the resonant frequency of ^{57}Fe is reached.

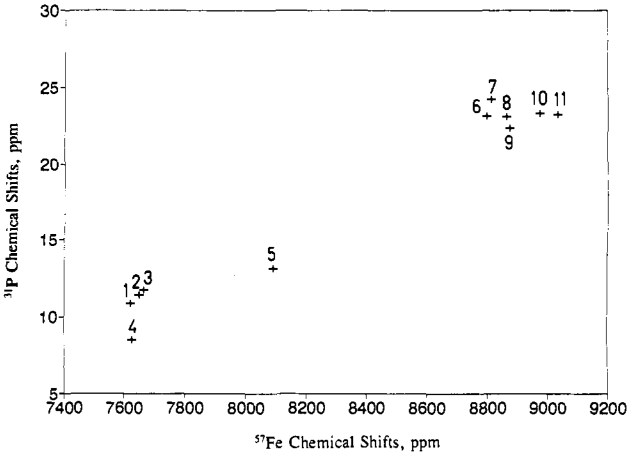

Figure 2. Correlation between ^{31}P and ^{57}Fe chemical shifts at 21 °C in C_6D_6, with ^{57}Fe shifts relative to external 90% $Fe(CO)_5$ in C_6D_6 and ^{31}P shifts relative to external 85% H_3PO_4: $[(p\text{-}Cl)_4TPPFe(PMe_3)_2]$ (1); $[TPPFe(PMe_3)_2]$ (2); $[(p\text{-}OCH_3)_4TPPFe(PMe_3)_2]$ (3); [TPPFe(PMe)(CO)] (4); [TPPFe(PMe_3)(*n*-BuNC)] (5); [TPPFe(PMe_3)(*n*-BuNH_2)] (6); [TPPFe(PMe_3)($PhCH_2SCH_3$)] (7); [TPPFe(PMe_3)(NMeIm)] (8); [TPPFe(PMe_3)(4-NMe_2Py)] (9); [TPPFe(PMe_3)(Py)] (10); [TPPFe(PMe_3)(4-CNPy)] (11).

We have applied the 1D indirect method utilizing the sensitive ^{31}P nucleus as the detected signal to a series of model hemes of the type $[(RTPP)^{57}Fe(PMe_3)(L)]$[15-19] (RTPP = a symmetrical, R–substituted tetraphenylporphyrin, L = PMe_3, CO, isonitrile, aliphatic amine, imidazole, pyridine, or thioether). The coordination of one or two phosphine ligands to the axial positions of Fe(II) model hemes has allowed us to determine ^{57}Fe chemical shifts of new complexes by decoupling the ^{57}Fe–^{31}P doublet of enriched ^{57}Fe(II) porphyrins, as shown in Figure 1. While it might be expected that finding the proper ^{57}Fe frequency to

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