

Push-Pull Porphyrins as Non-Linear Optical Materials

Chin-Ti Chen

Final Seminar


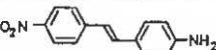


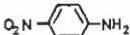
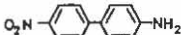
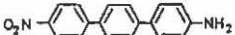
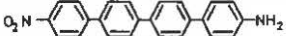
April 15, 1992

Porphyrins and metalloporphyrins provide a versatile synthetic base from which to design molecules with specific physical and chemical properties. The successes of such molecular engineering include the design of reversible O₂ binders [1], shape selective catalysts [2], molecular receptors [3], one-dimensional conductors and semiconductors [4], and models for the photosynthetic reaction center [5]. The development of metalloporphyrins as materials with electric, magnetic or optical field-responsive properties, however, has been extremely limited. We have been interested in the exploration of porphyrin and metalloporphyrin assemblies as ferroelectric [6] and as non-linear optical materials. Molecules with non-linear optical (NLO) properties have been extensively investigated due to their potential applications for optical communication, data storage, and electrooptical signal processing [7].

Donor-acceptor unsymmetrically substituted porphyrins, H₂(an₃Por), H₂(*cis*-a₂n₂Por), and H₂(a₃nPor) (where a = *p*-aminophenyl; n = *p*-nitrophenyl; Por = 5,10,15,20-substituted porphyrin) have been prepared with ≈25% isolate yield each. The synthesis does not involve the traditional cross-condensation for multi-substituted porphyrins, which usually results in low yield (<10%). Instead, these porphyrins were synthesized through the incomplete reduction of four nitro substituents on H₂(n₄Por) by SnCl₂ in concentrated HCl. Products were separated by chromatography and fully characterized by various spectroscopic methods.

Their second-order non-linear optical properties have been measured by the electric field-induced second-harmonic generation (EFISH) technique [8] giving second-order molecular hyperpolarizability (β) in the range of 10 to 30 × 10⁻³⁰ esu (see table below). The β values of these "push-pull" porphyrins are substantial and are comparable to those of nitro and amino substituted biphenyl and terphenyl compounds. The hyperpolarizabilities, however, are relatively small considering the total size of the π system of porphyrins. This is due to the shape of the π -conjugation of porphyrins. In addition, the dihedral twist of the phenyl groups out of the porphyrin plane may further inhibit efficient intramolecular charge-transfer (ICT) across the porphyrin ring between the donor and acceptor groups.

EFISH ($\lambda = 1908$ nm) DATA OF PUSH-PULL PORPHYRINS

Compound (in CHCl ₃)	μ (10 ⁻¹⁸ esu)	β (10 ⁻³⁰ esu)	Compound (in CHCl ₃)	μ (10 ⁻¹⁸ esu)	β (10 ⁻³⁰ esu)
I 	1.5 ^a	0.55 ^a	VII 	5.1	40
II 	4.0 ^a	1.9 ^a	VIII 	9	190 ± 50
III 	6.2 ^b 7.8 ^c	9.2 ^b 10 ^c			
IV 	5.0 7.8 ^c	24 24 ^c	H ₂ (an ₃ Por)		≤10
V 	7.6 ^c	16 ^c	H ₂ (<i>cis</i> -a ₂ n ₂ Por)	7 ± 1	30 ± 10
VI 	10 ^c	11 ^c	H ₂ (a ₃ nPor)	5 ± 1	20 ± 10

a. neat b. in acetone c. in NMP

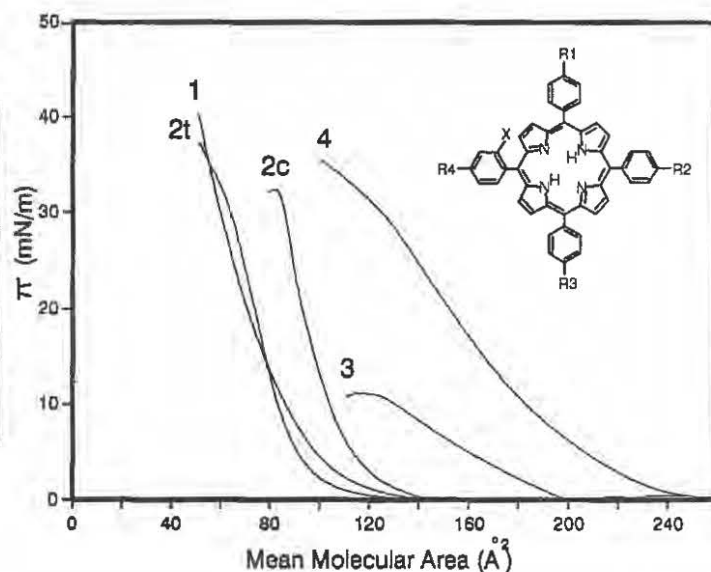
Moderate to strong solvatochromic effects have been observed in several *cis* isomers of "push-pull" porphyrins, H₂(*cis*-a₂n₂Por), H₂[*cis*-(Ocd_a)₂n₂Por], and H₂[*cis*-h₂(Ocd_{py})₂Por]-(I)₂ [where Ocd_a = *p*-(N-octadecylamino)phenyl; h = *p*-hydroxyphenyl; Ocd_{py} = *p*-(N-octadecyl)pyridiniumyl]. This is also an indication of the existence of ICT in these porphyrins.

^1H NMR can detect the non-symmetric ring current on *cis* isomers of "push-pull" porphyrins. The relative polarization of their π -electron density can be ordered as $\text{H}_2[\text{cis-h}_2(\text{Ocdpy})_2\text{Por}]^{2+} \approx \text{H}_2[\text{cis-m}_2(\text{Mpy})_2\text{Por}]^{2+} > \text{H}_2[\text{cis}-(\text{Ocda})_2\text{n}_2\text{Por}] \approx \text{H}_2[\text{cis-a}_2\text{n}_2\text{Por}] > \text{H}_2[\text{cis-h}_2\text{py}_2\text{Por}] \approx \text{H}_2[\text{cis-m}_2\text{py}_2\text{Por}] > \text{H}_2[\text{cis}-(s\text{-Clprmd})_2\text{n}_2\text{Por}] - \text{H}_2[\text{cis}-(\text{Ocdmd})_2\text{n}_2\text{Por}]$ (where Mpy = *p*-N-methylpyridiniumyl; py = *p*-pyridyl; m = *p*-methoxyphenyl; *s*-Clprmd = *p*-(*s*-2-chloropropionylamido)phenyl; Ocdmd = *p*-(octadecanoylamido)phenyl).

A wide range of β -active derivatives were prepared from $\text{H}_2(\text{a}_x\text{n}_{4-x}\text{Por})$. Particularly, those with hydrophobic moieties are used in Langmuir-Blodgett films. The isotherms (see figure below) of the first complete set of amphiphilic porphyrins, *i.e.*, $\text{H}_2[(\text{Ocdmd})_x\text{n}_{4-x}\text{Por}]$, with various numbers (*i.e.*, $x = 1$ to 4) of aliphatic chain substituents were studied [9]. We found that porphyrins with one or two aliphatic substituents adopt a perpendicular orientation to the water surface with A_0 (the mean molecular area extrapolated to zero pressure) less than 120 \AA^2 ; those with three or four aliphatic substituents have a parallel orientation to the water surface with $A_0 > 190 \text{ \AA}^2$. We were successful in aligning the *cis* isomer of "push-pull" porphyrins in a monolayer with a perpendicular orientation to the water surface. The mean molecular area of $\text{H}_2[\text{cis}-(\text{Ocdmd})_2\text{n}_2\text{Por}]$, $\text{H}_2[\text{cis}-(\text{Ocda})_2\text{n}_2\text{Por}]$, and $\text{H}_2[\text{cis-h}_2(\text{Ocdpy})_2\text{Por}](\text{NO}_3)_2$ were found to be 112 ± 5 , 108 ± 5 , and $142 \pm 5 \text{ \AA}^2$, respectively, in Langmuir films. Second-order non-linear optical susceptibilities ($\chi^{(2)}$) can be expected from such monolayers.

amd = $\text{NHC}(\text{CH}_2)_{16}\text{CH}_3$

R1	R2	R3	R4	X	name	$A_0(\text{\AA}^2/\#)$
NO_2	NO_2	NO_2	amd	H	1	89
NO_2	amd	NO_2	amd	Cl	2t	93
NO_2	NO_2	amd	amd	H	2c	105
NO_2	amd	amd	amd	H	3	199
amd	amd	amd	amd	H	4	210



References

- Collman, J. P.; Halbert, T. R.; Suslick, K. S. in *Metal Ion Activation of Dioxygen*; Spiro, T. G., Ed., Wiley: New York, 1980; Chapter 1.
 - Suslick, K. S.; Fox, M. M. *J. Am. Chem. Soc.* **1983**, *105*, 3507-3510.
 - Suslick, K. S.; Reinert, T. J. *J. Chem. Ed.* **1985**, *62*, 974-983..
 - Morgan, B.; Dolphin, D. *Struct. Bond.* **1987**, *64*, 115-203.
- Cook, B. R.; Reinert, T. J.; Suslick, K. S. *J. Am. Chem. Soc.* **1986**, *108*, 7281-8286.

- (b) Groves, J. T.; Neumann, R. *J. Am. Chem. Soc.* **1989**, *111*, 2900-2909.
- (c) Suslick, K. S. in *Activation and Functionalization of Alkanes*; Hill, C. L., Ed., Wiley: New York, 1989, pp. 219-241.
3. Lehn, J.-M. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 89-112.
4. (a) Collman, J. P.; McDevitt, J. T.; Leidner, C. R.; Yee, G. T.; Torrance, J. B.; Little, W. A. *J. Am. Chem. Soc.* **1987**, *109*, 4606-4614.
- (b) Hanack, M.; Deger, S.; Lange, A. *Coord. Chem. Rev.* **1988**, *83*, 115-136.
- (c) Marks, T. J. *Angew Chem. Int. Ed. Engl.* **1990**, *29*, 857-879.
- (d) Godfrey, M. R.; Newcomb, T. P.; Hoffman, B. M.; Ibers, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 7260-7269.
5. (a) Connolly, J. S.; Bolton, J. R. in *Photoinduced Electron Transfer*, Fox, M. A.; Chanon, M., Eds., Elsevier: Amsterdam, 1988, Vol. D, pp 303-393.
- (b) Gust, D.; Moore, T. A.; Moore, A. L.; Gao, F.; Luttrull, D. K.; DeGraziano, J. M.; Ma, X. C.; Markings, L. R.; Lee, S.-J.; Trier, T. T.; Bittersmann, E.; Seely, G. R.; Woodward, S.; Bensasson, R. V.; Rougee, M.; De Schryver, F. C.; Van der Auweraer, M. *J. Am. Chem. Soc.* **1991**, *112*, 3638-3649.
6. (a) Suslick, K. S.; Chen, C.-T. *Polym. Mater. Sci. Eng.* **1990**, *63*, 272-276.
- (b) Suslick, K. S.; Chen, C.-T., "One-Dimensional Coordination Polymers," *Coord. Chem. Rev.*, in preparation.
7. (a) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991.
- (b) Stucky, G. D.; Marder, S. R.; Sohn, J. E., Eds., *Materials for Nonlinear Optics*; ACS Symposium Series 233; American Chemical Society: Washington, D.C., 1991.
- (c) Hann, R. A.; Bloor, D., Eds., *Organic Materials for Nonlinear Optics II*; Royal Society of Chemistry: London, 1991.
- (d) Eaton, D. F.; Meredith, G. R.; Miller J. S. *Adv. Mater.* **1992**, *4*, 45-48.
8. Suslick, K. S.; Chen, C.-T.; Meredith, G. R.; Cheng, L.-T., "Push-Pull Porphyrins as Non-linear Optical Materials," *J. Am. Chem. Soc.* **1992**, *114*, in press.
9. Suslick, K. S.; Chou, H.; Chen, C.-T.; Bohn, P. W.; Stork, K. F., "Langmuir-Blodgett Films of Push-Pull Porphyrins," in preparation.