Supporting Information

A Self-Assembled Light-Harvesting Array of Seven Porphyrins in a Wheel and Spoke Architecture

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Static absorption and fluorescence measurements were performed on non-deaerated samples in toluene or $CHCl_3$ at room temperature as described previously.[1] Absorption spectra were collected using a Hewlett-Packard HP 8453 spectrometer (1 nm data points). Fluorescence spectra were collected using a Spex Fluoromax (1 nm data points, 1 mm slit widths, 4.25 nm spectral bandpass). The $CHCl_3$ (inhibited with amylenes) was stored over Na_2CO_3 prior to use. Fluorescence emission yields were measured by comparison of integrated corrected spectra with tetraphenylporphyrin (Φ_f = 0.11) or zinc tetraphenylporphyrin (Φ_f = 0.033) in toluene as a standard.[2] Fluorescence yield determinations in $CHCl_3$ led to values of 0.10(6) or 0.030 for tetraphenylporphyrin or zinc tetraphenylporphyrin, respectively.

Mass spectra of porphyrins were obtained via laser desorption mass spectrometry (LD-MS) in the absence of an added matrix[3] (Bruker Proflex II instrument) and by high resolution fast atom bombardment (FAB) on a JEOL (Tokyo, Japan) HX 110HF mass spectrometer. Tri-*o*-tolylphosphine and tris(dibenzylideneacetone)dipalladium(0), [$Pd_2(dba)_3$], were used as received from Aldrich.

The studies to determine association constants for binding of the guests (**1**, **2**) and the hosts (*cyclo*-Zn_6U, *cyclo*-Zn_3Fb_3U) were performed using absorption spectroscopy at room temperature. Solutions of equimolar amounts of host and guest were prepared at ~3-4 x 10^{-7} M, examined for association (positive control), and then diluted by 10-fold. At 3-4 x 10^{-8} M the absorption in the Soret region was slightly less than 0.1. Multicomponent analysis, employing spectra of bound and unbound species as the limiting forms, was performed to establish a lower limit on the association constant. In the two cases examined by dilution experiments (*cyclo*-Zn_3Fb_3U–**1**, *cyclo*-Zn_6U–**2**) the amount of unbound species was < 25% at 3-4 x 10^{-8} M, implying an association constant > 3 x 10^8 M^{-1}. (The spectral change upon forming *cyclo*-Zn_6U–**1** was nearly identical to that with Zn_3Fb_3U–**1**.) Accurate determination of binding constants would require work in the more dilute concentration regime (<10^{-8} M) where binding is less pronounced. The acquisition of meaningful absorption spectra in such dilute solutions (A_{Soret} < 0.03; 1-cm pathlength cell) would require signal averaging of static absorption spectra. While such studies are beyond the scope of this paper, the bounds established on the association constants by the binding studies performed are sufficient to demonstrate the utility of these self-assembled structures for light-harvesting applications. The structures and symbolic representations of the self-assembled arrays are shown in Figure 1.

5,15-Bis{4-[2-(4-pyridyl)ethynyl]phenyl}-10,20-dimesitylporphyrin (2). Following a standard method for Pd-mediated coupling,[4] samples of 5,15-bis(4-iodophenyl)-10,20-dimesitylporphyrin[5] (95.1 mg, 100 μmol), 4-ethynylpyridine[6] (30.9 mg, 300 μmol), $Pd_2(dba)_3$ (55.0 mg, 60 μmol) and P(*o*-tol)$_3$ (146 mg, 480 μmol) were weighed into a 50 mL Schlenk flask. (Note: the amounts of the Pd catalyst and ligand used in this coupling reaction were doubled as compared with the typical stoichiometric ratio[4] of iodo, ethyne, $Pd_2(dba)_3$ and P(*o*-tol)$_3$ species because the typical amount of catalyst gave the desired product in only 16% yield.) The flask

was evacuated and purged with argon three times (care must be taken to avoid the loss of 4-ethynylpyridine by vacuum sublimation) and then degassed toluene/triethylamine (24 mL, 5:1) was added by syringe. The flask was immersed in an oil bath at 35 °C and the contents were stirred under argon. The reaction was followed by LD-MS and TLC analysis (silica gel, $CHCl_3$/MeOH, 97:3). After 2 h, no starting porphyrin was observed, however, a significant amount of the mono-coupled byproduct was observed (LD-MS obsd at *m/z* = 928.0, calcd 925.9 for $C_{57}H_{44}IN_5$). Additional 4-ethynylpyridine (10.3 mg, 100 μmol) was added under argon and the reaction was continued. After stirring at 35 °C overnight, LD-MS analysis of the crude reaction mixture showed only a minor amount of the mono-coupled product. (Note: The reaction can be followed either by TLC ($CHCl_3$/MeOH, 97:3) or LD-MS analysis, however, LD-MS analysis of the crude mixture was more effective in identifying the progress of the reaction. The reaction cannot be followed by analytical SEC due to the close retention times of the starting porphyrin, product and the mono-coupled byproduct; in fact, analytical SEC always gave a broad single peak comprising all of the porphyrins.) The solvent was removed, then the residue was dissolved in a minimum amount of $CHCl_3$/MeOH (97:3) and loaded on a silica gel column. Elution with $CHCl_3$/MeOH (97:3) gave the mono-coupled product (confirmed by LD-MS analysis) followed by the desired product as the second band. The solvent was removed and the residue was placed on top of a cotton plug in a Pasteur pipette. After washing with MeOH, the purple material on top of the cotton plug was dissolved in $CHCl_3$, concentrated and dried, affording a purple solid (41.5 mg, 46%). ^{1}H NMR ($CDCl_3$) δ 8.80 (d, 4H, *J* = 4.5 Hz, β-pyrrole), 8.73 (d, 4H, *J* = 4.5 Hz, β-pyrrole), 8.70 (d, 4H, *J* = 6.0 Hz, pyridyl-H), 8.26 (d, 4H, *J* = 7.8 Hz, ArH), 7.95 (d, 4H, *J* = 7.8 Hz, ArH), 7.53 (d, 4H, *J* = 6.0 Hz, pyridyl-H), 7.29 (s, 4H, ArH), 2.64 (s, 6H, Me), 1.84 (s,12H, Me), -2.63 (s, br, 2H, NH); LD-MS obsd 902.1, calcd 900.4 ($C_{64}H_{48}N_6$); λ_{abs} (log ε) in $CHCl_3$ (nm) 422 (5.61), 517 (4.29), 552 (4.03), 592 (3.80), 647 (3.72);

λ_{em} (λ_{ex} 550 nm) 651, 717 nm ($\Phi_f = 0.13$). See attached ^{1}H NMR and LD-MS spectra.

References:

(1) (a) Hsiao, J.-S.; Krueger, B. P.; Wagner, R. W.; Delaney, J. K.; Mauzerall, D. C.; Fleming, G. R.; Lindsey, J. S.; Bocian, D. F.; Donohoe, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 11181-11193. (b) Strachan, J. P.; Gentemann, S.; Seth, J.; Kalsbeck, W. A.; Lindsey, J. S.; Holten, D.; Bocian, D. F. *J. Am. Chem. Soc.* **1997**, *119*, 11191-11201. (c) Yang, S. I.; Seth, J.; Balasubramanian, T.; Kim, D.; Lindsey, J. S.; Holten, D.; Bocian, D. F. *J. Am. Chem. Soc.* **1999**, *121*, 4008-4018.

(2) Seybold, P. G.; Gouterman, M. *J. Mol. Spectroscopy* **1969**, *31*, 1-13.

(3) (a) Fenyo, D.; Chait, B. T.; Johnson, T. E.; Lindsey, J. S. *J. Porphyrins Phthalocyanines* **1997**, *1*, 93-99. (b) Srinivasan, N.; Haney, C. A.; Lindsey, J. S.; Zhang, W.; Chait, B. T. *J. Porphyrins Phthalocyanines* **1999**, *3*, 283-291.

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(5) Littler, B. J.; Ciringh, Y.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 2864-2872.

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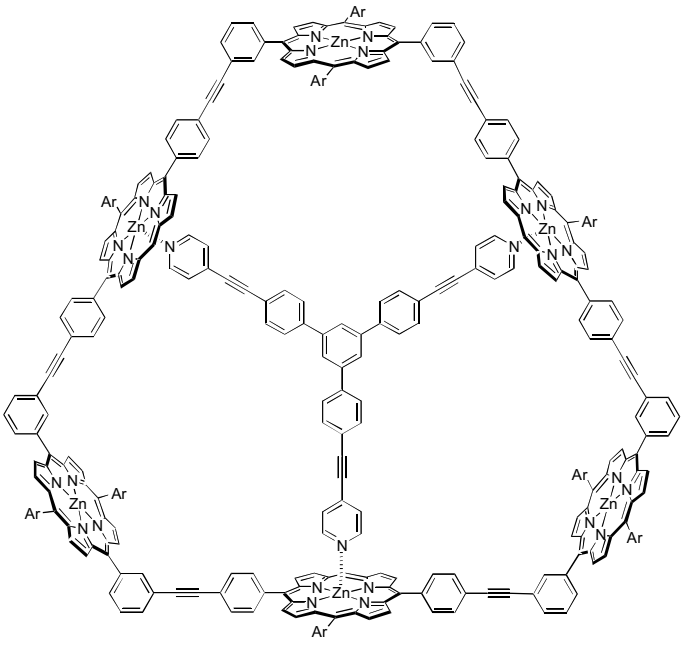
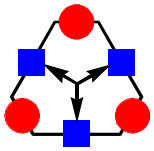
Figure 1.

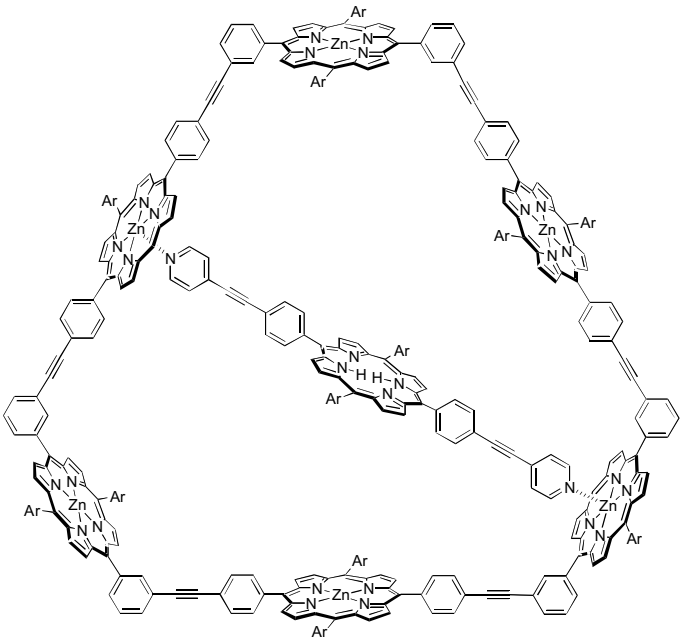


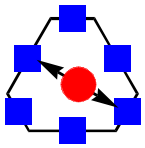


symbolic representation

***cyclo*-Zn$_6$U-1** Ar = mesityl

In both structures, a mesityl group is present at each non-linking meso position. Mesityl groups are not displayed on templated porphyrins for visual clarity.

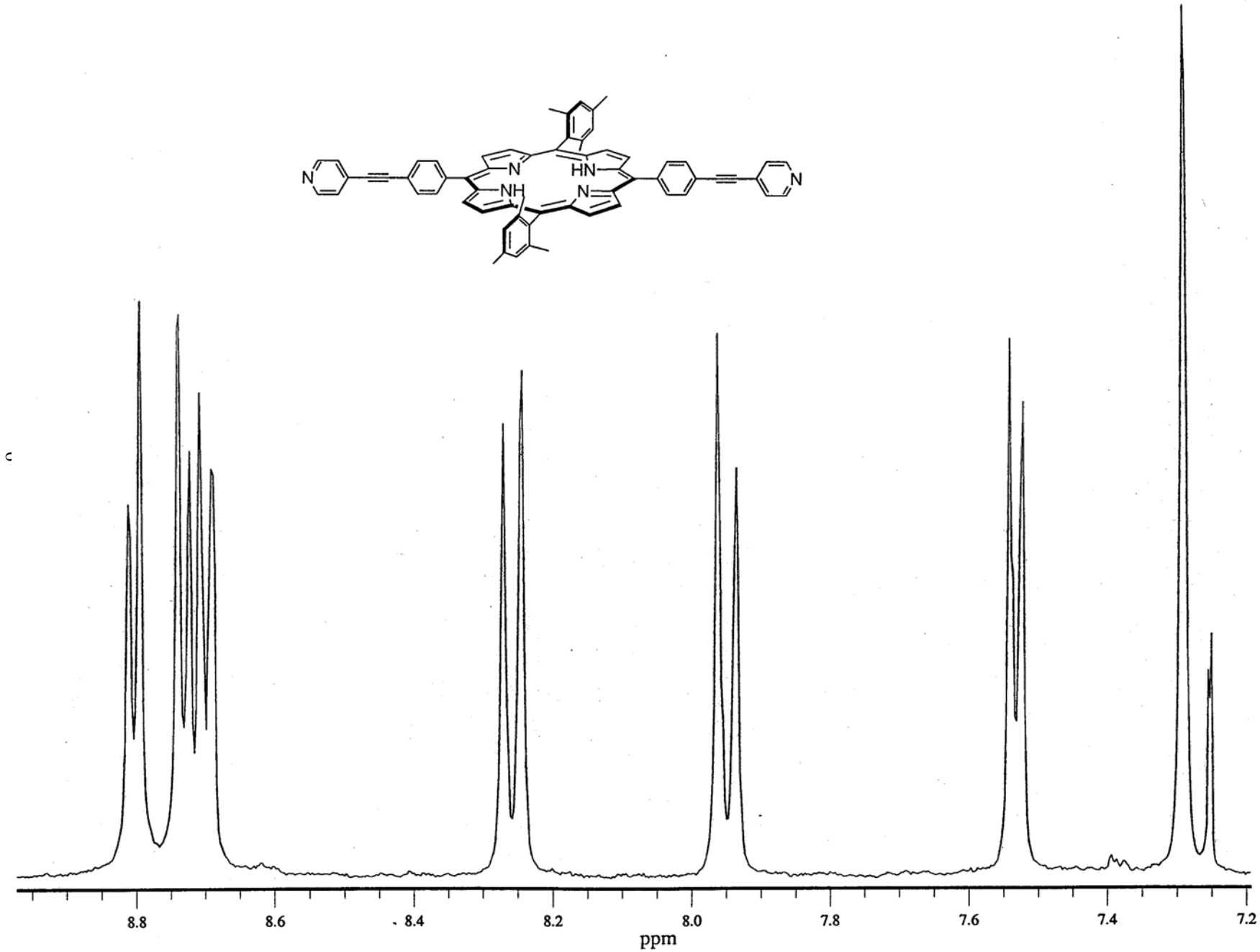




symbolic representation

***cyclo*-Zn$_6$U-2** Ar = mesityl

Note the off-center positioning of the free base porphyrin guest due to the meta,meta or para,para substitution pattern of the diphenylethyne unit on the respective coordinated zinc porphyrins in the cyclic host.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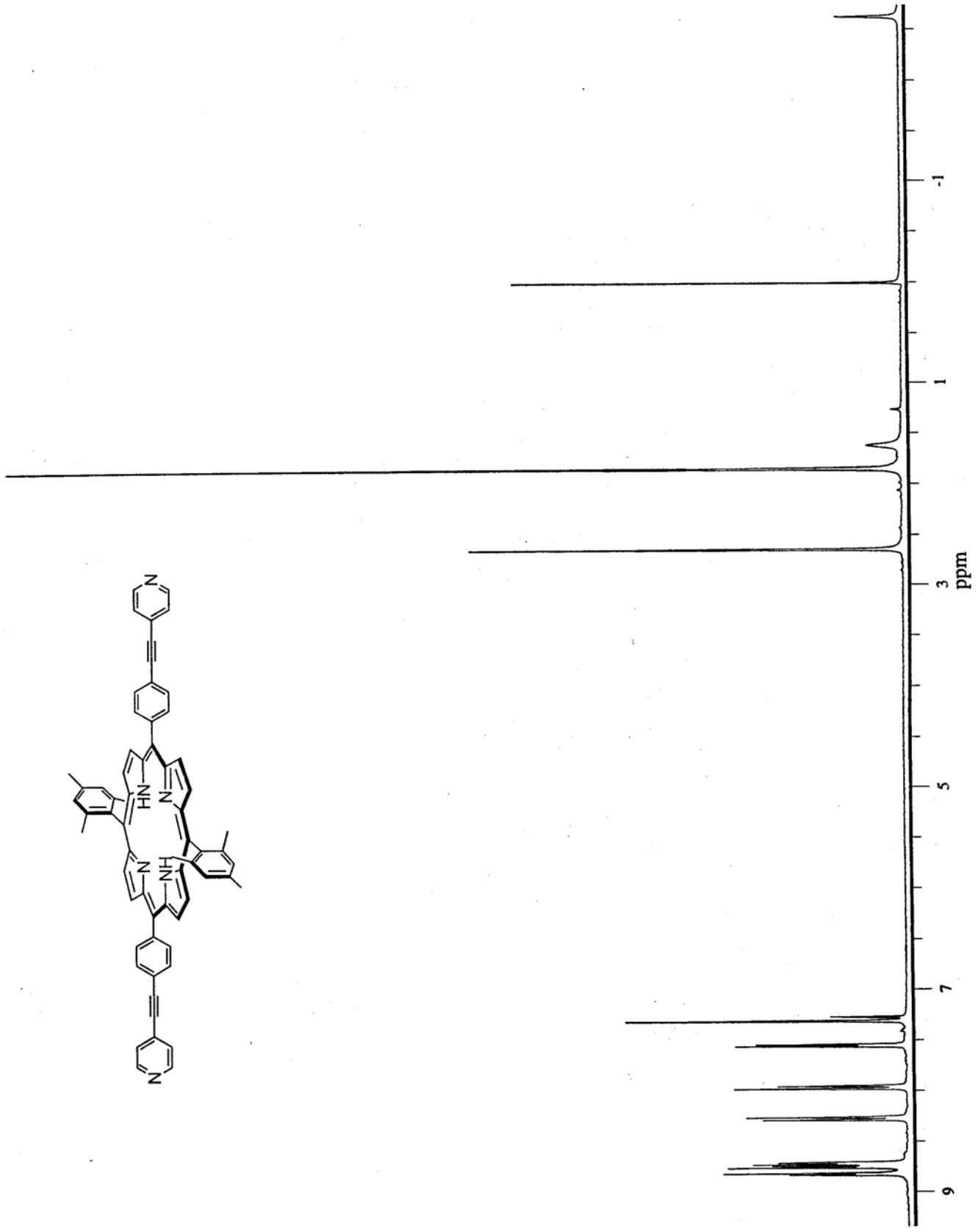
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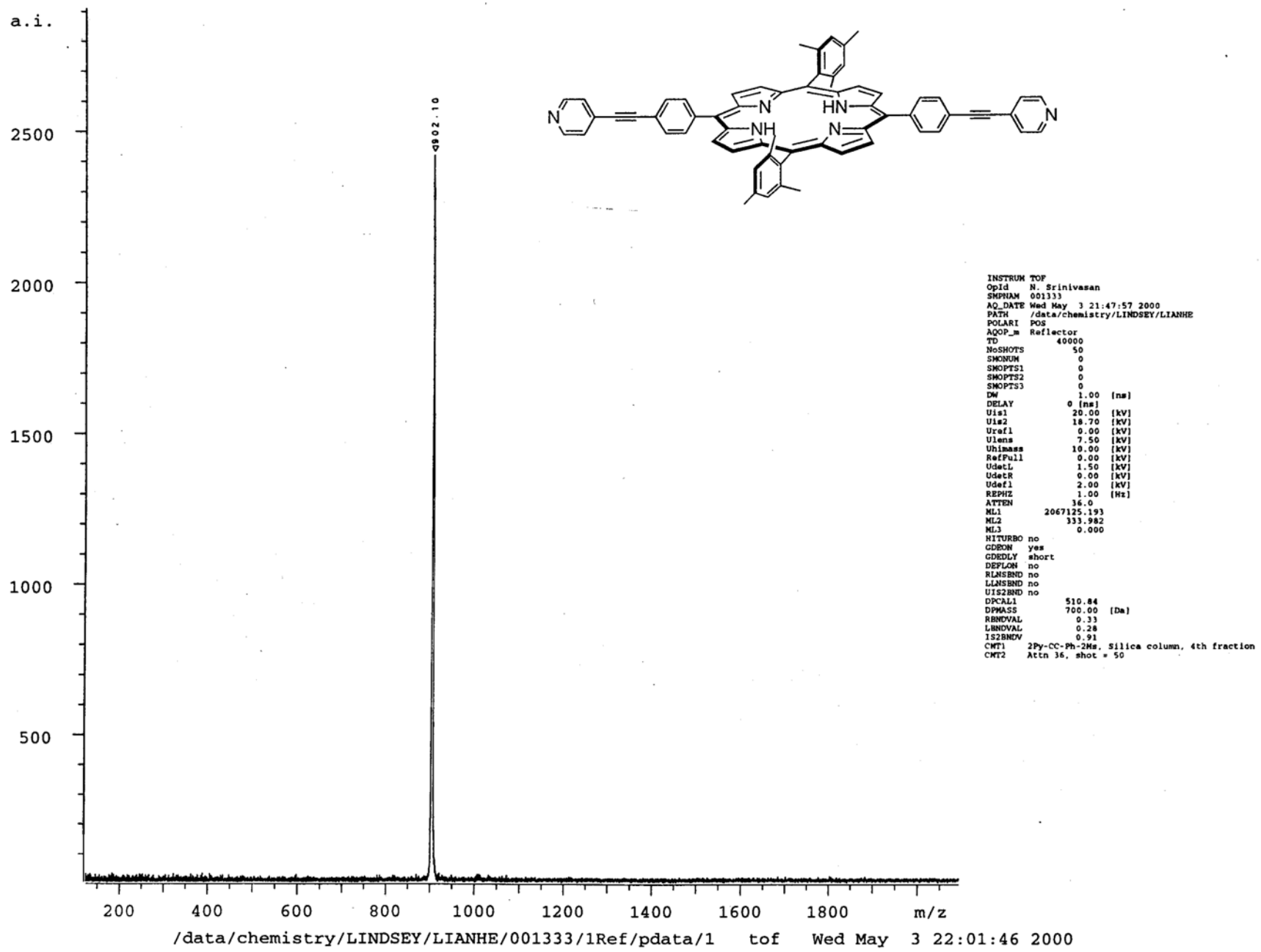

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