Supporting information for:

Monomeric, not tetrameric species are responsible for the colossal dielectric constant of the copper phthalocyanine derived from pyromellitic dianhydride

Gellert Mezei,* Andre R. Venter, Joseph W. Kreft, Alexander A. Urech and Nicole R. Mouch
Western Michigan University, Department of Chemistry, Kalamazoo, MI 49008, USA.

1. Experimental details

All commercially available reagents and solvents (Sigma-Aldrich) were used as received. UV-Vis spectra were recorded at room temperature on a Shimadzu UV 2101 PC spectrophotometer, in aqueous 0.1 M NaOH (**1a** and **1b**) or chloroform solutions (**2**). Mass spectral data were recorded in negative mode up to m/z 4000 with a linear ion trap mass spectrometer (LTQ; Thermo Scientific, Waltham, MA, USA), equipped with an Ion Max electrospray ionization source. Samples were infused by a syringe pump at 5 µL/min and nitrogen was supplied as nebulizing gas at a setting of 12 arbitrary units. The electrospray voltage was set to –4.2 kV spray voltage. The transfer capillary was maintained at a desolvation temperature of 200°C and 25 V while the tube lens was set to 160 V. Solutions were prepared at 10^{-5} M concentrations in dimethylformamide (**1a** and **1b**) or chloroform (**2**).

2. Details of the mass spectrometric analysis

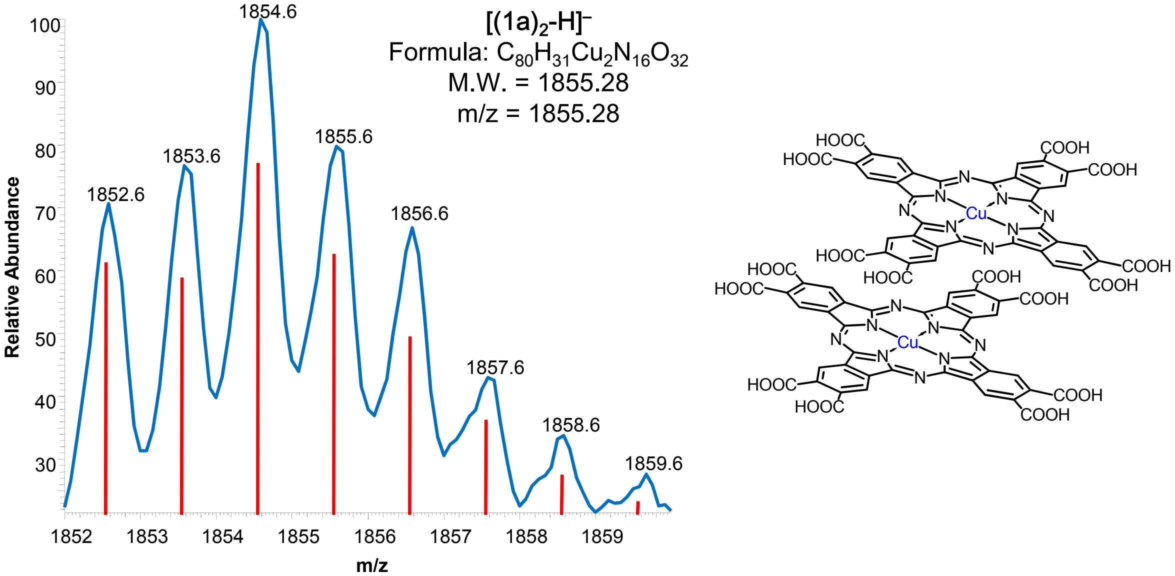


Figure S1. Predicted (red) and observed (blue) isotopic pattern for $[(\mathbf{1a})_2\text{–H}]^-$.

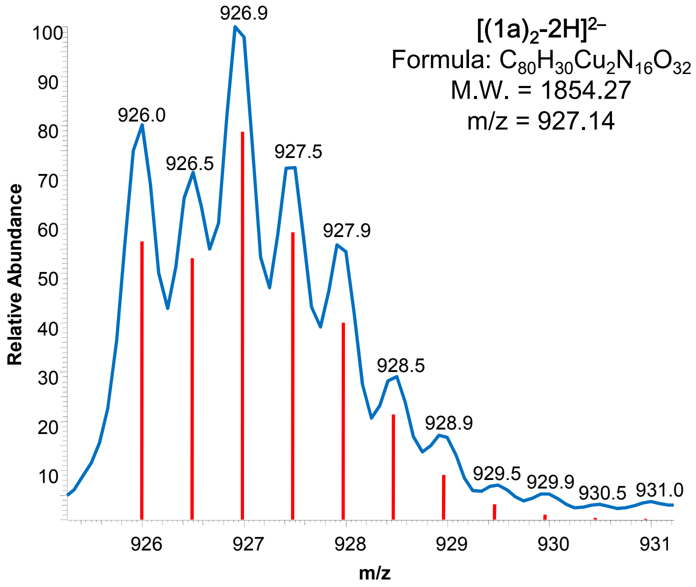


Figure S2. Predicted (red) and observed (blue) isotopic pattern for $[(\mathbf{1a})_2–2H]^{2–}$.

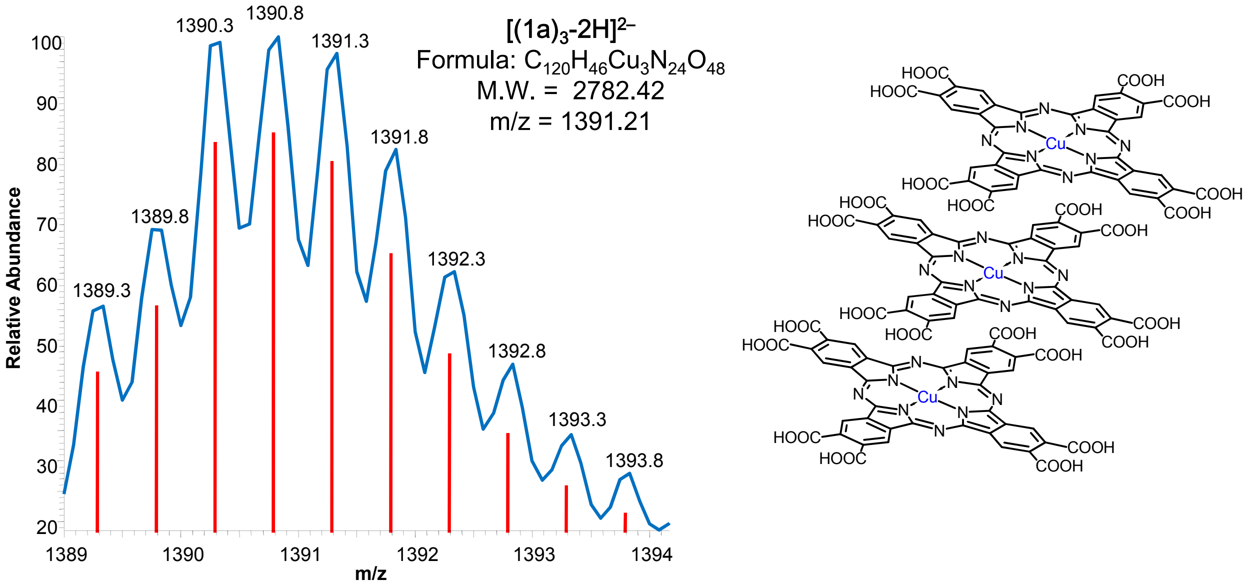


Figure S3. Predicted (red) and observed (blue) isotopic pattern for $[(\mathbf{1a})_3–2H]^{2–}$.

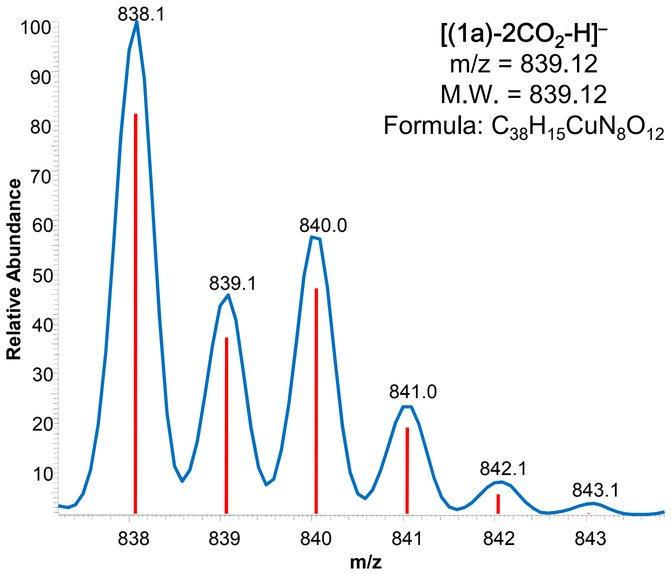


Figure S4. Predicted (red) and observed (blue) isotopic pattern for [(**1a**)–2CO$_2$–H]$^-$.

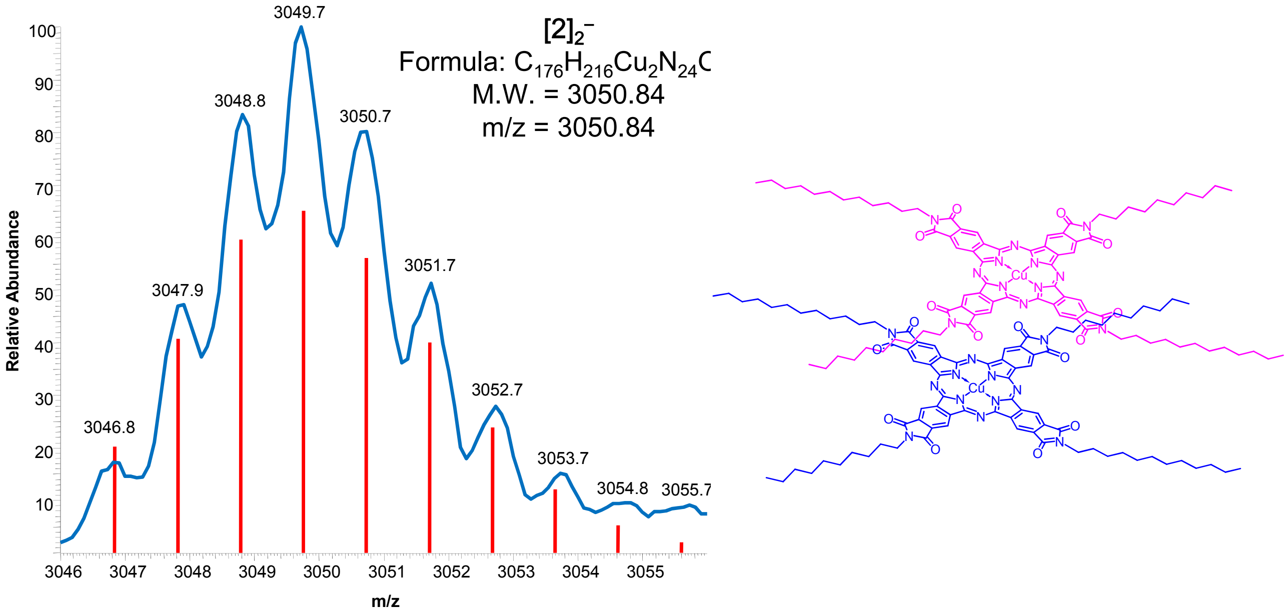


Figure S5. Predicted (red) and observed (blue) isotopic pattern for [**2**]$_2^-$.

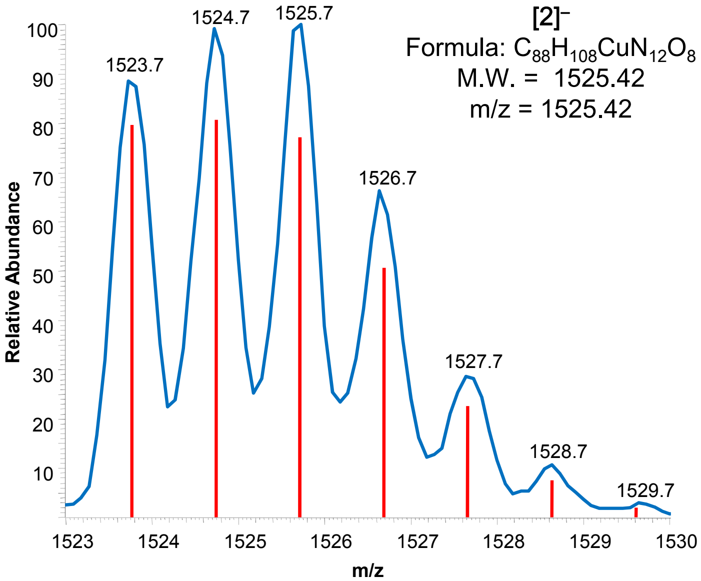


Figure S6. Predicted (red) and observed (blue) isotopic pattern for [**2**]⁻.

3. Literature survey of the phthalocyanines obtained from pyromellitic acid derivatives.

Phthalocyanines (Pc) were discovered over a century ago[1] and constitute approximately a quarter of all artificial organic pigments used nowadays,[2] with copper phthalocyanine (CuPc, Figure S7) being the single largest-volume colorant produced.[3] Besides its high tinctorial properties, CuPc also possesses semiconductivity, photoconductivity and catalytic properties, and it is one of the most widely used materials in organic field-effect transistor[4] and organic solar cell research.[5] The synthesis, characterization and applications of phthalocyanines are thoroughly reviewed.[6] Polymeric phthalocyanines became interesting research targets following the discovery of the high thermal and chemical stability of the phthalocyanine ring. Polymers containing phthalocyanine units linked by ether bridges were prepared as early as 1958,[7,8] however polymers with fused phthalocyanines were sought for achieving even greater stability and improved physico-chemical properties due to extended conjugation/resonance.

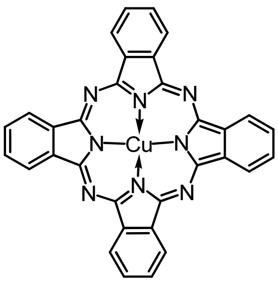


Figure S7. Structure of the parent copper phthalocyanine (CuPc).

In 1958, Marvel and Rassweiler,[7] and in 1959, Drinkard and Bailar[9] reported the use of pyromellitic dianhydride (PMDA) fused with urea and copper chloride (and ammonium molybdate as catalyst) at 160-180 °C in the presence or absence of 1,2-dichlorobenzene as solvent, in an attempt to prepare large graphite-like sheets of phthalocyanine polymers. Using elemental analysis and end group (carboxylic acid) titration, they concluded that the reaction product contains linear oligomers with up to six Pc units, and no evidence was found for even the smallest sheet oligomer proposed, a 2×2 array of four fused phthalocyanines. In 1960, Epstein and Wildi fused 1,2,4,5-tetracyanobenzene (pyromellitonitrile, PMN), CuCl and urea at 350 °C under 1000 psi N_2 pressure to prepare a copper phthalocyanine "polymer", and studied its electrical properties (variable temperature Hall effect and electrical resistivity).[10] In 1965, Inoue et al. reported similar conditions (along with a modified procedure using ethylene glycol solvent at 180-200 °C) to prepare mixed copper/iron "polymers", which acted as oxidation catalysts.[11-14] The known synthesis methods and properties of "polymeric" phthalocyanines and their metal complexes were first reviewed in 1971.[15] A year later, in 1972, Bailar's group reported that only the monomeric $(CuPc)(CN)_8$ is obtained when PMN is used instead of PMDA, in ethylene glycol solvent at 180-200 °C.[16] They also showed that the use of different PMDA:urea:$CuCl_2$ ratios and different reaction temperatures (180-250 °C) leads to the isolation of either the monomeric $(CuPc)(COOH)_8$, or the impure dimer and linear tetramer and pentamer, respectively, with varying degrees of hydration. However, it was also noted that the copper content of the oligomeric species was in general significantly lower than the expected values. In 1974, Norrell et al. reported the use of PMN and urea at 450° to prepare Cu, Fe, Sb and Zn phthalocyanine "polymers", and studied the electronic conduction and polarization within those materials.[17] Bailar's PMDA method was used by Kreja et al.[18,19] and Blomquist et al.[20-22] to prepare "polymeric" iron phthalocyanines. In 1980, Wöhrle et al. showed that only the monomeric phthalocyanine is obtained from PMN when 1-propanol or N,N-dimethylaminoethanol are used as solvent,[23] and showed that the resulting octacyanophthalocyanine $(CuPc)(CN)_8$ can be converted to the corresponding carboxylic acid, anhydride, imido and amido derivatives.[24] In 1981, Nalwa et al. reported the synthesis and electrical properties of a "polymeric" iron Pc obtained using PMDA in the presence of nitrobenzene solvent at 200 °C.[25] Using the same method, in 1982 Achar et al. reported the preparation and characterization of Cu, Ni and Co analogs.[26] Contrary to previous observations, they assigned the product to a pure cyclic tetramer ("sheet oligomer", $(Cu_4Pc^*)(COOH)_{16}$), based on IR spectroscopy, elemental and titrimetric analyses. Shortly afterwards, in 1983 Nalwa et al. reproduced Bailar's synthesis[16] using the conditions that were reported to lead to a "pentamer dihydrate", and found that the electrical resistivity of the resulting material (which they considered to be the tetrameric sheet oligomer) is affected by washing with various solvents or chemical solutions.[27] In 1985, Lin et al. used PMN and CuCl in 1-methyl-2-pyrrolidone (NMP) at ~150 °C to obtain a CuPc "polymer",[28] and showed that thermal treatment leads to large electrical conductivity.[29] Copper phthalocyanine "polymers" have also been obtained by the reaction of PMN with copper metal.[30-34] In the same year, Wöhrle et al. carried out an extensive analysis of Bailar's PMDA method reported in 1972,[16] and concluded that reaction times of 60 minutes and temperatures of 270 °C are optimal for the preparation of Cu, Co, Ni, Fe and Mg phthalocyanine "polymers" from various pyromellitic acid derivatives and excess urea, without the use of a solvent.[35-37] They concluded (based on elemental analysis) that these "polymers" contain at least 9 Pc units. Also in 1985, Nalwa et al. reported that the CuPc "polymer" obtained by using Bailar's PMDA method[16] (again, considered to be the cyclic fused tetramer) has an extremely high dielectric constant.[38] Following these discoveries, a series of papers exploring the desirable properties attributed to "phthalocyanine tetramers" were published.[39-50] Composite materials incorporating "phthalocyanine tetramers" mixed with organic polymers[51-59] or grafted onto organic polymers[60-66] or nanoparticles[67] were also prepared, culminating with the publication of a paper in *Nature*.[68] With one exception using a modification (boric acid as catalyst) of Bailar's PMDA method,[45] all these papers reference the method of Achar et al.[26] for the preparation of the "tetrameric" $(Cu_4Pc^*)(COOH)_{16}$, and they all attribute the high dielectric constant to the extended conjugated system of this "sheet oligomer".

4. Comments on elemental analysis results of "oligomeric" copper phthalocyanines

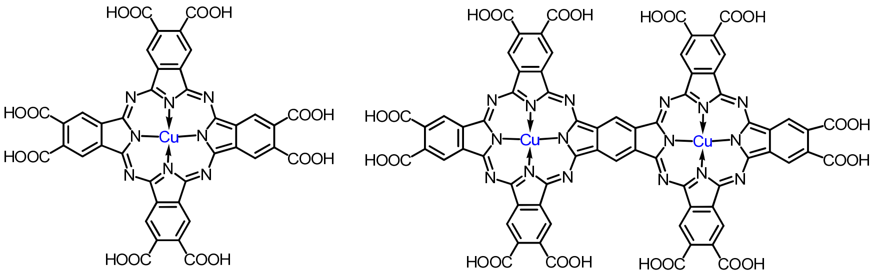
From the very first attempts of assigning a structure to the phthalocyanines derived from PMDA, by using elemental analysis, Bailar et al. were confronted with grossly low copper contents (as put by the authors themselves).[16] For example, only 5.40% Cu instead of an expected 8.21% was found for the assumed "tetramer dihydrate". Since the C, H, N analyses were in good agreement with the expected values, the low copper content was attributed to partial demetallation of the phthalocyanine rings. This seems a rather odd assumption, considering that excess copper was used in the preparation of those compounds, and no conditions that could apparently lead to cleavage of the strong Cu–N bonds of the phthalocyanine complexes were employed. In fact, later it was reported that the use of harsh conditions for the saponification of the peripheral imide to carboxylic acid groups, such as a boiling 50% KOH solution, leads not to demetallation, but to the total breakdown of the phthalocyanine scaffold.[35] This observation was also confirmed in our laboratory, when a sudden, total loss of the characteristic deep blue-purple color of the copper phthalocyanine compound was observed during saponification under the above conditions. The resultant white solid was found to be the potassium salt of pyromellitic acid.

A comparative analysis of the expected elemental composition of the mononuclear and various oligonuclear copper(II) phthalocyanine complexes reveals rather insignificant differences (often within experimental error) between their corresponding C, H and N contents. Table S1 shows the calculated C, H, N and Cu contents of the monomer and fused dimer, trimer, and linear and cyclic tetramers (Figure S8), along with the reported values for the carboxylic acid and the corresponding anhydride derivative of the assumed[26] “cyclic tetramer”.

Significant deviations of the reported values from the calculated ones for both the “cyclic tetramer” and its assumed octahydrate are observed. Although the observed values for the corresponding anhydride derivative seem to be closer to the calculated ones (except for N),[26] Wöhrle et al. later showed that the carboxylic acid derivative does not completely dehydrate to the anhydride before thermal decomposition occurs upon heating in vacuum above 400 °C.[35] Moreover, other researchers employing Achar’s method also found low Cu content for the corresponding potassium salt of the assumed “tetramer” (6.08 % instead of the calculated 7.42 %).[62] Various amounts of absorbed water or oxygen have often been considered in an attempt to reconcile observed with calculated values. Therefore, it appears that elemental analysis is not a reliable method for characterizing these types of materials.

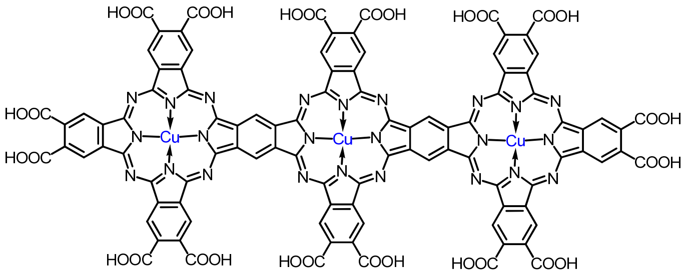
Table S1. Calculated (black) and reported (red) C, H, N and Cu contents of carboxylated CuPc derivatives (Fig. S8).

CuPc oligomer	**C (%)**	**H (%)**	**N (%)**	**Cu (%)**
Carboxylic acid derivative				
monomer	51.76	1.74	12.07	6.85
dimer	52.48	1.64	13.99	7.93
trimer	52.77	1.59	14.77	8.38
tetramer (linear)	52.93	1.57	15.19	8.62
tetramer (cyclic)	53.46	1.50	16.63	9.43
tetramer (cyclic) + 8 H_2O	50.75	1.99	15.78	8.95
Reported values[26]	48.62	2.48	14.12	8.80
Anhydride derivative				
monomer	56.12	0.94	13.09	7.42
dimer	56.27	0.94	15.00	8.51
trimer	56.34	0.95	15.77	8.94
tetramer (linear)	56.37	0.95	16.18	9.18
tetramer (cyclic)	56.48	0.95	17.56	9.96
Reported values[26]	56.26	1.20	19.97	10.02

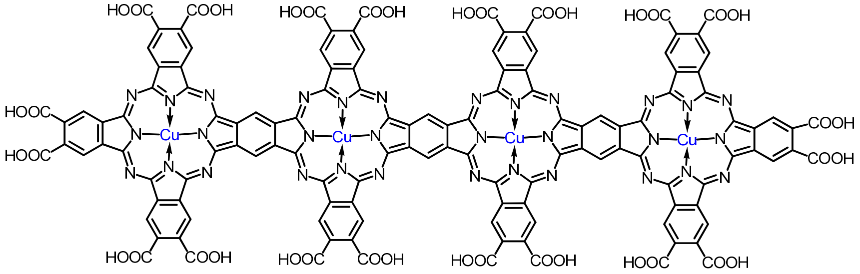


monomer

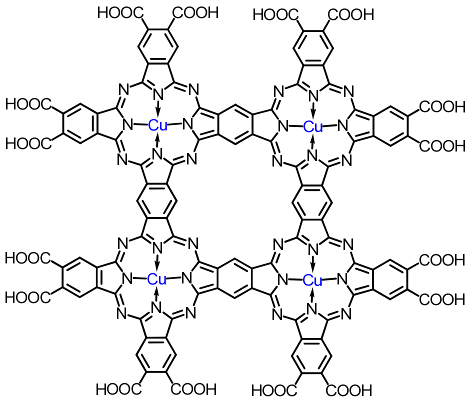
dimer



trimer



tetramer (linear)



tetramer (cyclic)

Figure S8. Structures of the carboxylated CuPc monomer and hypothetical fused dimer, trimer and tetramers.

4. References

[1] A. Braun, J. Tcherniac, *Ber. Dtsch. Chem. Ges.,* 1907, **40**, 2709.
[2] G. Löbbert, "Phthalocyanines" in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, 2002.
[3] P. Gregory, *J.Porphyrins Phthalocyanines,* 2000, **4**, 432-437.
[4] G. Chaidogiannos, F. Petraki, N. Glezos, S. Kennou and S. Nešpůrek, *Appl.Phys. A,* 2009, **96**, 763-767.
[5] M. G. Waltera, A. B. Rudineb and C. C. Wamser, *J. Porphyrins Phthalocyanines,* 2010, **14**, 759-792.
[6] "The Porphyrin Handbook", Vols. 15-20, K. M. Kadish, K. M. Smith and R. Guilard (Eds.), Academic Press, 2003.
[7] C. S. Marvel and H. H. Rassweiler, *J. Am. Chem. Soc.,* 1958, **80**, 1197-1199.
[8] C. S. Marvel and M. M. Martin, *J. Am. Chem. Soc.,* 1958, **80**, 6600-6604.
[9] W. C. Drinkard and J. C. Bailar, Jr., *J. Am. Chem. Soc.,* 1959, **81**, 4795-4797.
[10] A. Epstein and B. S. Wildi, *J. Chem. Phys.,* 1960, **32**, 324-329. Erratum: *J. Chem. Phys.,* 1960, **33**, 618.
[11] H. Inoue, Y. Kida and E. Imoto, *Bull. Chem. Soc. Japan***,** 1965, **38**, 2214.
[12] H. Inoue, Y. Kida and E. Imoto, *Bull. Chem. Soc. Japan,* 1967, **40**, 184-190.
[13] H. Inoue, Y. Kida and E. Imoto, *Bull. Chem. Soc. Japan,* 1968, **41**, 684-691.
[14] H. Inoue, Y. Kida and E. Imoto, *Bull. Chem. Soc. Japan,* 1968, **41**, 692-696.
[15] A. A. Berlin and A. I. Sherle, *Inorg. Macromol. Rev.,* 1971, **1**, 235-270.
[16] D. R. Boston and J. C. Bailar, Jr., *Inorg. Chem.,* 1972, **11**, 1578-1583.
[17] C. J. Norrell, H. A. Pohl, M. Thomas and K. D. Berlin, *J. Polym. Sci. B: Polym. Phys.,* 1974, ***12***, 913-924.
[18] L. Kreja and A. Plewka, *Electrochim. Acta,* 1980, **25**, 1283-1286.
[19] L. Kreja and A. Plewka, *Angew. Makromolec. Chem.,* 1982, **102**, 45-48.
[20] J. Blomquist, L. C. Moberg, L. Y. Johansson and R. Larsson, *J. Inorg. Nucl. Chem.,* 1981, **43**, 2287-2292.
[21] J. Blomquist, U. Helgeson, L. C. Moberg, L. Y. Johansson and R. Larsson, *Electrochim. Acta,* 1982, **27**, 1445-1451.
[22] J. Blomquist, U. Helgeson, L. C. Moberg, L. Y. Johansson and R. Larsson, *Electrochim. Acta,* 1982, **27**, 1453-1460.
[23] D. Wöhrle, G. Meyer and B. Wahl, *Makromol. Chem.,* 1980, **181**, 2127-2135.
[24] D. Wöhrle and U. Hündorf, *Makromol. Chem.,* 1985, **186**, 2177-2187.
[25] H. S. Nalwa, J. M. Sinha and P. Vasudevan, *Makromol. Chem.,* 1981, **182**, 811-816.
[26] B. N. Achar, G. M. Fohlen, J. A. Parker, *J. Polym. Sci. A: Polym. Chem. Ed.,* 1982, **20**, 1785.
[27] H. S. Nalwa and P. Vasudevan, *J. Mater. Sci. Lett.,* 1983, **2**, 77-79.
[28] J. W.-P. Lin and L. P. Dudek, *J. Polym. Sci.: Polym. Chem. Ed.,* 1985, **23**, 1579-1587.
[29] J. W.-P. Lin and L. P. Dudek, *J. Polym. Sci.: Polym. Chem. Ed.,* 1985, **23**, 1589-1597.
[30] R. Bannehr, G. Meyer and D. Wöhrle, *Polym. Bull.,* 1980, **2**, 841-846.
[31] D. Wöhrle, R. Bannehr, B. Schumann, G. Meyer and N. Jaeger, *J. Mol. Catal.,* 1983, **21**, 255-263.
[32] D. Wöhrle, M. Kirschenmann and N. I. Jaeger, *J. Electrochem. Soc.,* 1985, **132**, 1150-1152.
[33] M. Yudasaka, K. Nakanishi, T. Hara, M. Tanaka and S. Kurita, *Jap. J. Appl. Phys.,* 1985, **24**, L887-L889.
[34] D. Wöhrle, V. Schmidt, B. Schumann, A. Yamada and K. Shigehara, *Ber. Bunsenges. Phys. Chem.,* 1987, **91**, 975-981.
[35] D. Wöhrle and E. Preußner, *Makromol. Chem.,* 1985, **186**, 2189-2207.
[36] D. Wöhrle, U. Marose and R. Knoop, *Makromol. Chem.,* 1985, **186**, 2209-2228.
[37] D. Wöhrle and B. Schulte, *Makromol. Chem.,* 1985, **186**, 2229-2245.
[38] H. S. Nalwa, L. R. Dalton and P. Vasudevan, *Eur. Polym. J.,* 1985, **21**, 943-947.
[39] S. Venkatachalam, K. V. C. Rao, P. T. Manoharan, *Synth. Met.,* 1988, **26**, 237-246.
[40] U. S. Tewari and S. K. Sharma, *Tribology Int.,* 1989, **26**, 253-258.

[41] S. Venkatachalam, K. V. C. Rao and P. T. Manoharan, in "*Frontiers of Polymer Research*", P. N. Prasad and J. K. Nigam (eds), Plenum Press, New York, 1991, pp. 431-436.
[42] S. Venkatachalam, K. V. C. Rao and P. T. Manoharan, *Polym. Sci.,* 1991, **2**, 727-734.
[43] S. Venkatachalam and P. V. Prabhakaran, *Eur. Polym. J.,* 1993, **29**, 711-714.
[44] S. Venkatachalam, K. V. C. Rao and P. T. Manoharan, *J. Polym. Sci. B: Polym. Phys.,* 1994, **32**, 37-52.
[45] M. A. Abd El-Ghaffar, E. A. M. Youssef, N. R. El-Halawany and M. A. Ahmed, *Angew. Makromolec. Chem.,* 1998, **254**, 1-9.
[46] S. Saravanan, C. J. Mathai, M. R. Anantharaman, S. Venkatachalam and P. V. Prabhakaran, *J. Appl. Polym. Sci.,* 2004, **91**, 2529-2535.
[47] V. Bobnar, A. Levstik, C. Huang and Q. M. Zhang, *Phys. Rev. B,* 2005, **71**, 041202(R).
[48] S. Sagar, S. Saravanan, S. S. Kumar, S. Venkatachalam and M. R. Anantharaman, *J. Phys. D: Appl. Phys.,* 2006, **39**, 1678-1683.
[49] J. Bijwe and N. Phougat, *J. Porphyrins Phthalocyanines,* 1998, **2**, 223-230.
[50] U. S. Tewari, S. K. Sharma, H. S. Nalwa and P. Vasudevan, *IEEE Trans. Electr. Insul.,* 1985, **EI-20**, 975-977.
[51] S. Venkatachalam, T. M. Vijayan and S. Packirisamy, *Makromol. Chem., Rapid Commun.,* 1993, **14**, 703-706.
[52] H. Xu, Y. Bai, V. Bharti and Z.-Y. Cheng, *J. Appl. Polym. Sci.,* 2001, **82**, 70-75.
[53] C. Huang, Q. M. Zhang, G. deBotton and K. Bhattacharya, *Appl. Phys. Lett.,* 2004, **84**, 4391-4393.
[54] V. Bobnar, A. Levstik, C. Huang and Q. M. Zhang, *Phys. Rev. Lett.,* 2004, **92**, 047604.
[55] C. Huang, Q. M. Zhang, J. Y. Li and M. Rabeony, *Appl. Phys. Lett.,* 2005, **87**, 182901.
[56] S. Saravanan, M. R. Anantharaman and S. Venkatachalam, *Mater. Sci. Eng. B,* 2006, **135**, 113-119.
[57] V. Bobnar, A. Levstik, C. Huang and Q. M. Zhang, *Ferroelectrics,* 2006, **338**, 107-116.
[58] S. Zhang, C. Huang, R. J. Klein, F. Xia, Q. M. Zhang and Z.-Y. Cheng, *J. Intell. Mater. Syst. Struct.,* 2007, **18**, 133-145.
[59] J. Zhang, D. Zhu and M. Matsuo, *J. Polym. Sci. B: Polym. Phys.,* 2009, **47**, 1146-1155.
[60] J.-W. Wang, Q.-D. Shen, C.-Z. Yang and Q.-M. Zhang, *Macromolecules,* 2004, **37**, 2294-2298.
[61] J.-W. Wang, Q.-D. Shen, H.-M. Bao, C.-Z. Yang and Q.-M. Zhang, *Macromolecules,* 2005, **38**, 2247-2252.
[62] C. Huang and Q. M. Zhang, *Adv. Mater.,* 2005, **17**, 1153-1158.
[63] Y. Wang, J.-W. Wang, F. Wang, S. Li and J. Xiao, *Polym. Bull.,* 2008, **60**, 647-655.
[64] J.-W. Wang, Y. Wang, F. Wang, S.-Q. Li, J. Xiao and Q.-D. Shen, *Polymer,* 2009, **50**, 679-684.
[65] J.-W. Wang, Y. Wang, S.-Q. Li and J. Xiao, *J. Polym. Sci. B: Polym. Phys.,* 2010, **48**, 490-495.
[66] R. Saha and B. K. Mandal, *J. Appl. Polym. Sci.,* 2010, **117**, 122-128.
[67] Z.-M. Dai, Y. Gao, H.-P. Xu and J. Bai, *J. Colloid Interface Sci.,* 2008, **322**, 491-496.
[68] Q. M. Zhang, H. Li, M. Poh, F. Xia, Z.-Y. Cheng, H. Xu and C. Huang, *Nature,* 2002, **419**, 284.