Electronic Supplementary Information for Dalton Transactions

Synthesis, characterization and nonlinear absorption of novel octakis-POSS substituted metallo phthalocyanines and strong optical limiting property of CuPc

Tanju Ceyhan,[a] Mustafa Yüksek,[b] H. Gül Yağlıoğlu,[b] Bekir Salih,[c] Mehmet K. Erbil[a], Ayhan Elmalı, *[b] and Özer Bekaroğlu*[d]

[a]Department of Biochemistry, Division of Organic Chemistry, Gülhane Medical Academy, (GATA), Ankara, Turkey. Fax: +90 312 3043300;
[b]Department of Engineering Physics, Faculty of Engineering, Ankara University, Ankara, Turkey. Fax: +90 312 2127343;
[c]Department of Chemistry, Hacettepe University, 06532 Ankara, Turkey. Fax: +90 312 2992163;
[d]Department of Chemistry,Technical University of Istanbul, 80626 Maslak, Istanbul, Turkey. Fax:+90 216 3860824;E-mail:obek@itu.edu.tr

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MALDI-MS Discussion

High resolved MALDI mass spectrum of the synthesized phthalonitrile derivative **3** was obtained using positive ion reflectron mode in dithranol matrix and the spectrum is given in Fig. 1A. HCl adduct of protonated molecular ion peak of **3** was observed at 1942-1950 Da nominal mass range. HCl affinity of this compound was observed very high and HCl was the intermediate product in the first step of the synthesis. The HCl adduct of protonated molecular ion peak of **3** was showed a broad range isotopic peak distribution and the peak masses was followed each other with one Da nominal mass difference because of the isotopic peaks of carbon, chlorine and silicon. These isotopic peak distributions were exactly overlapped with the mass of **3** calculated theoretically from the elemental composition of this compound and are given as inset spectrum. Beside the protonated molecular ion peak of the compound, two high intense peaks were observed and characterized leaving group from the whole molecule by the fragmentation on the carbon-sulphur bond. One fragment ion was the $C_{31}H_{69}O_{12}SSi_8$ and the second one was the other part of the structure without any excess fragmentation.

Positive ion and linear mode MALDI-MS spectra of synthesized Co(II)Pc **4** was obtained and is given in Fig. 1B. Beside the protonated molecular ion peak of cobalt complex observed at 7676 Da nominal mass, some other fragment ions at low masses compared to the mass of protonated molecular ion peak were also observed. The fragment ions were formed mainly from leaving bulky silicon and oxygen based groups. Low intense protonated molecular ion peak of **4** is because of the long mass range isotopic peak distribution and low stability of the protonated molecular ion peak of this high molecular weight compound.

Linear mode MALDI mass spectrum of Pc **5** and Pc **6** were obtained using positive mode in α-cyano-4-hydroxycinnamic acid matrix only compared the other novel MALDI matrices and the spectra are given in Fig. 2, Fig. 3, respectively. Protonated molecular ion peaks of Pc **5** and Pc **6** were observed at 7680 and 7682 Da mass ranges (Fig. 2 and Fig. 3). The nominal mass of these peaks were exactly correlated with the mass of copper and zinc complexes calculated theoretically from the elemental composition of the complex. To follow the protonated molecular ion peaks and their adducts, expanded form of the molecular mass regions were given

as inset spectrum. Beside the protonated molecular ion peak of the complexes, some high intense fragment peaks were observed and these peaks (on both complex spectra were identical) correlates some degradations from the whole complex at the breakable sides. All the fragment peaks were evaluated and found that the peaks were because of the fragmentation not the impurities in the complex samples. Although, these complexes were less stable but reasonably enough to follow the protonated molecular ion peaks under the laser firing and MALDI-MS conditions.

Figures

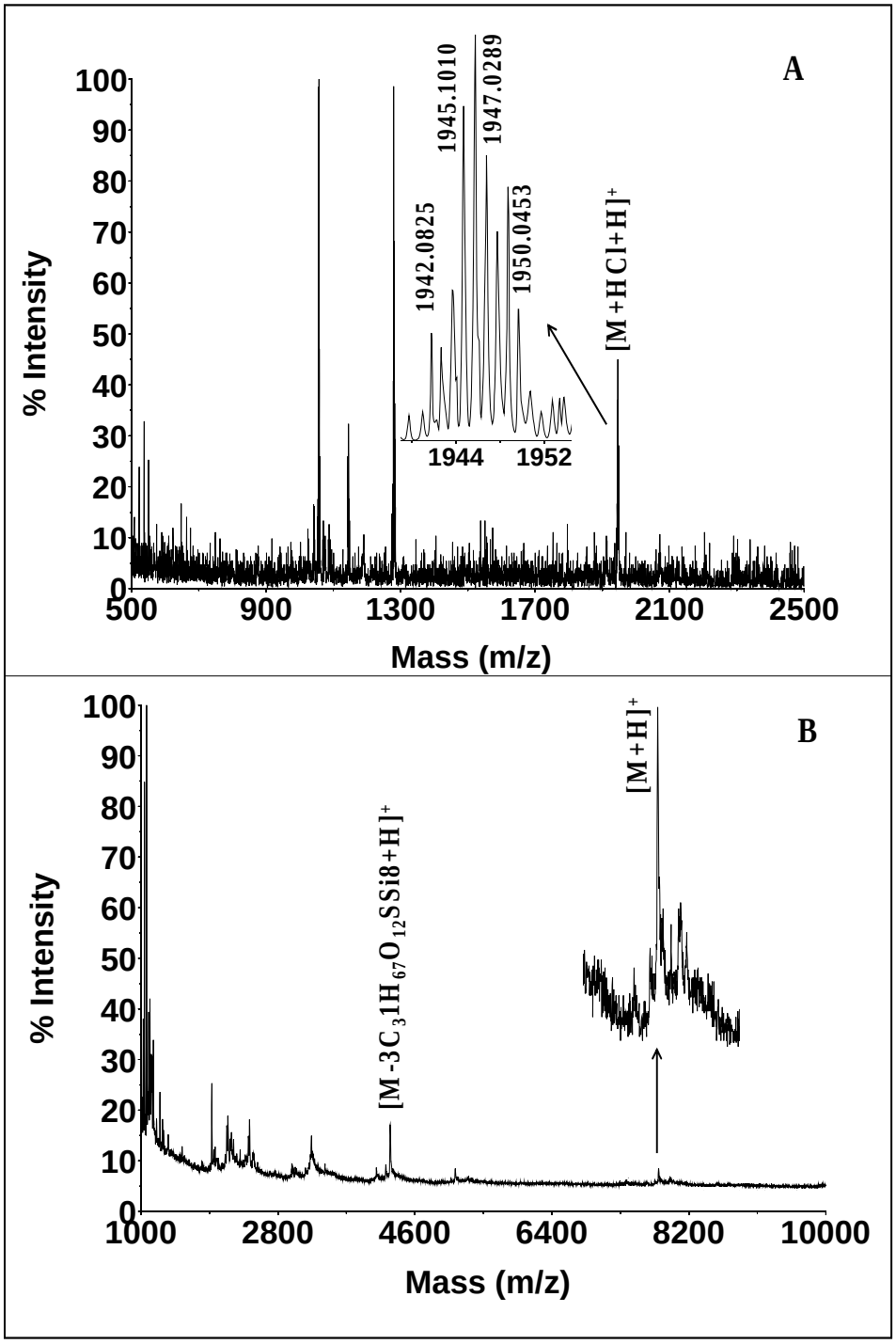

Fig.1. Positive ion MALDI-MS spectra of (A) synthesized intermediate ligand **3** having 1904 g/mol nominal mass and $C_{70}H_{140}O_{24}S_2N_2Si_{16}$ molecular formula obtained in reflectron mode, (B) Pc **4** which has 7675 g/mol nominal mass and $C_{280}H_{560}O_{96}S_8Si_{64}N_8$obtained in linear mode. Dithranol (1,8-dihydroxy-10H-anthracen-9-one) (20 mg/mL tetrahydrofuran) MALDI matrix was used and 50 laser shots were accumulated using nitrogen laser. Inset spectrum shows expanded molecular mass region of **3** and Pc **4**.

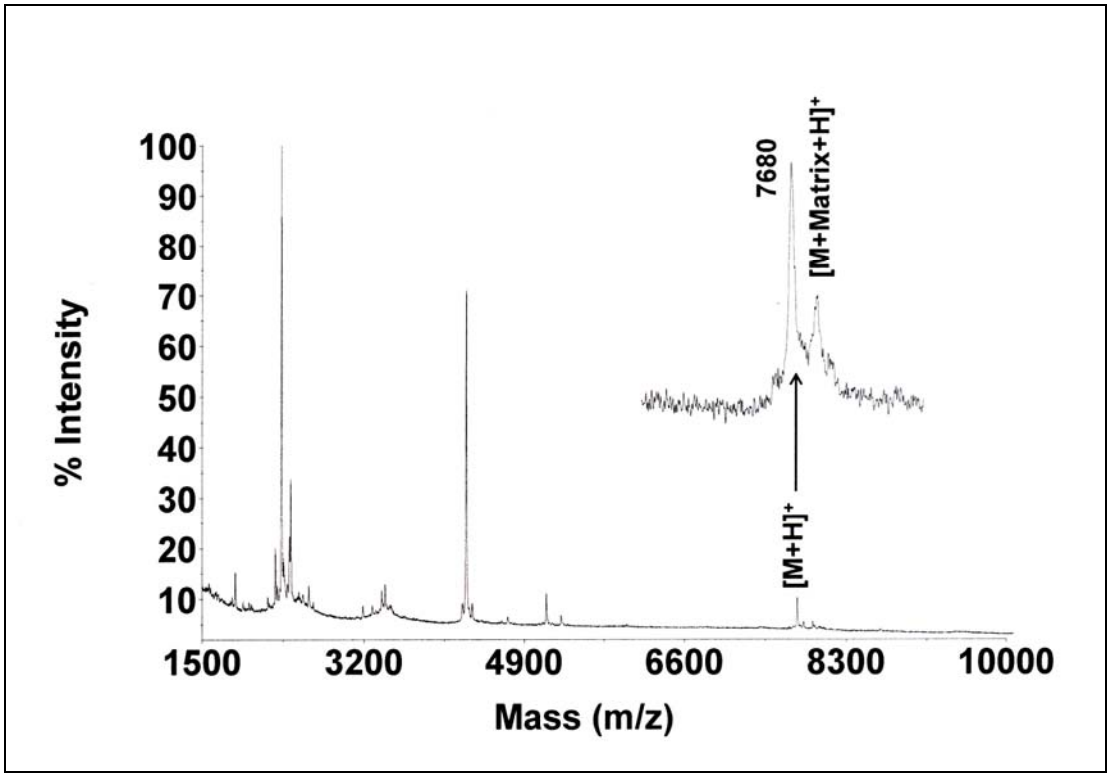

Fig 2. Positive ion mode MALDI-MS spectrum of Pc **5** was obtained in α-cyano-4-hydroxycinnamic acid (15 mg/mL acetonitril-water, 1:1) MALDI matrix using nitrogen laser accumulating 100 laser shots. Inset spectrum shows expanded molecular mass region of Pc **5**.

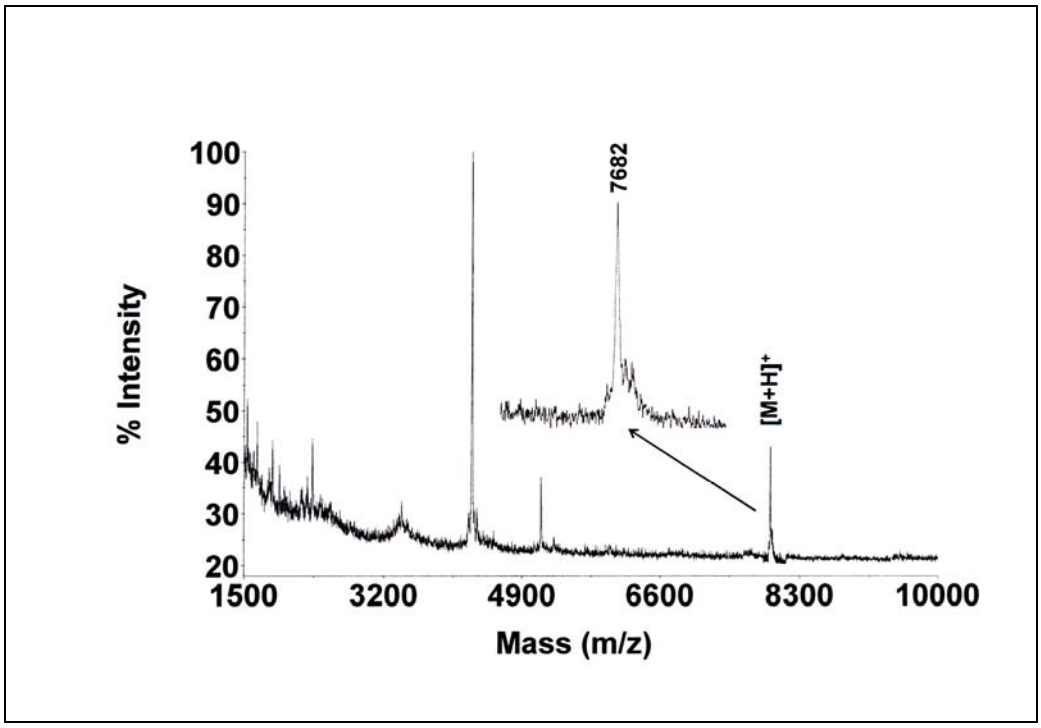

Fig 3. Positive ion mode MALDI-MS spectrum of Pc **6** was obtained in α-cyano-4-hydroxycinnamic acid (15 mg/mL acetonitril-water, 1:1) MALDI matrix using nitrogen laser accumulating 100 laser shots. Inset spectrum shows expanded molecular mass region of Pc **6**.