DOI: 10.1002/adsc.200900705

Binuclear Iron(III) Phthalocyanine(μ-Oxodimer)-Catalyzed Oxygenation of Aromatic Hydrocarbons with Iodosylbenzene Sulfate and Iodosylbenzene as the Oxidants

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Received: October 10, 2009; Published online: December 10, 2009

Abstract: Two binuclear iron(III) phthalocyanine-(μ-oxodimer) complexes were tested in catalytic oxygenation reactions of several aromatic hydrocarbons using iodosylbenzene $(PhIO)_n$ or oligomeric iodosylbenzene sulfate $[(PhIO)_3SO_3]_n$ as the oxidants. Results of this study demonstrate that $[(PhIO)_3SO_3]_n$ is the most reactive oxygenating reagent that can be used as a safe and convenient alternative to the thermally unstable and potentially explosive iodosylbenzene. The pyridine-containing binuclear μ-oxobis{iron(III)-pyridino[3,4]-9(10),16(17),23(24)-tri-*tert*-butyltribenzoporphyrazine} is significantly more active as compared to the traditional μ-oxobis[iron(III)-2,9(10),16(17),23(24)-tetra-*tert*-butylphthalocyanine].

Keywords: iodine; iodosylbenzene; iodosylbenzene sulfate; iron phthalocyanine μ-oxodimer; oxygenation

Introduction

The catalytical properties of transition metal porphyrins, phthalocyanines, and related compounds have been well-documented within the last 50 years.[1] As it was shown recently, porphyrin and phthalocyanine iron (III) μ-oxo-,[2a–c] and μ-nitrido-dimers,[2d,e] which were earlier considered as catalytically inactive compounds, in many cases have high catalytic activity in different oxidation reactions. Traditionally, hydrogen peroxide and organic peroxides were used as the oxidants for transition metal porphyrin-type-catalyzed reactions.[3] These oxidants, however, can be involved into parallel one- and two-electron transfer reactions, which often compromise the selectivity of catalytic reactions.

Hypervalent iodine compounds are versatile, selective oxidants that have the added advantage of being biodegradable and low in toxicity.[4,5] Among these reagents, iodosylbenzene, $(PhIO)_n$ (**1**) (Figure 1), is, probably, the mostly used oxygen transfer agent,[5] which has also found widespread application in various transition metal porphyrin catalyzed oxygenation reactions.[6] Despite its usefulness as an oxidant, practical applications of iodosylbenzene are hampered by its low solubility in non-reactive media,[5] as well as its low thermal stability and explosive properties upon moderate heating.[7] We have recently shown that the μ-oxobis[iron(III)-2,9(10),16(17),23(24)-tetra-*tert*-butylphthalocyanine] (**3**) is an effective catalyst for the oxidation of a variety of organic substrates with hypervalent iodine reagents.[8] In particular, the oligomeric iodosylbenzene sulfate $[(PhIO)_3SO_3]_n$ (**2**) was proven to be an excellent alternative to iodosylbenzene in transition metal phthalocyanine- and porphyrin-catalyzed reactions.

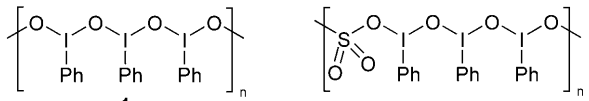

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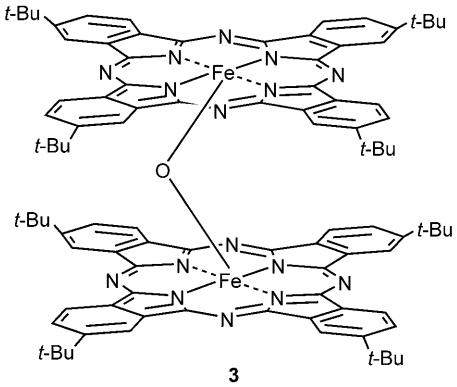
Figure 1. Hypervalent iodine oxidants: iodosylbenzene **1** and oligomeric iodosylbenzene sulfate **2**.

In this paper, we report preliminary results on comparative reactivity of the well-known compound **3** and new iron(III) phthalocyanine μ-oxodimer **4** (Figure 2) in the biomimetic oxidation of several aromatic compounds using traditional iodosylbenzene (**1**) and the new hypervalent iodine reagent **2** (Figure 1) as terminal oxidants.



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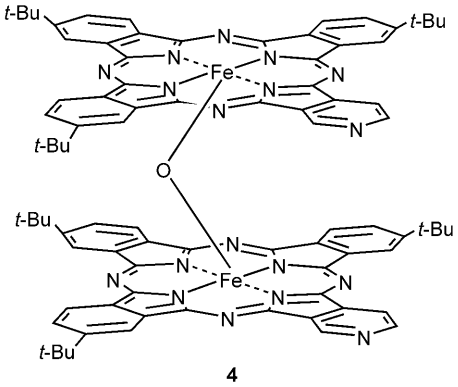

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Figure 2. Iron(III) phthalocyanine-(μ-oxodimer) **3** and **4**.

Results and Discussion

The oligomeric iodosylbenzene sulfate $[(PhIO)_3{\cdot}SO_3]_n$ **2** was prepared by simple treatment of commercially available (diacetoxyiodo)benzene with aqueous sodium hydrogen sulfate and isolated as a thermally stable, yellow crystalline solid.[8] Complex **3** was prepared using a direct high-temperature reaction between 4-*tert*-butylphthalonitrile and iron(II) acetate as described previously,[9] while preparation of the new catalyst **4** is based on the metallation reaction of asymmetric metal-free μ-oxobis[iron(III)-pyridino-[3,4]-9(10),16(17),23(24)-tri-*tert*-butyl-tribenzoporphyrazine] and is described in the Experimental Section. There are two main reasons for testing the catalyst **4**. First, the introduction of a fused pyridine ring into the phthalocyanine core increases its first oxidation potential. Second, the nitrogen atom of the pyridine ring can serve as an effective axial group, which can be coordinated to one iron(III) center thus increasing the electron density on the second iron(III) ion in **4**.

The results of the catalytic oxidation of anthracene **5**, 2-*tert*-butylanthracene **8**, 2-methylnaphthalene **12**, 9,10-phenanthrene **16**, and adamantane **20** using hy-

Table 1. Catalytic oxidations of aromatic hydrocarbons and adamantane using oxidants **1** and **2** and catalysts **3** and **4**.

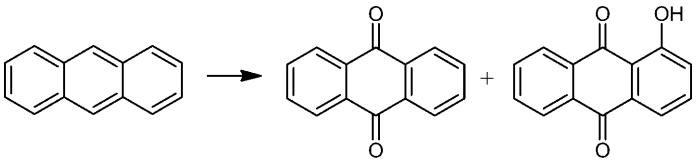
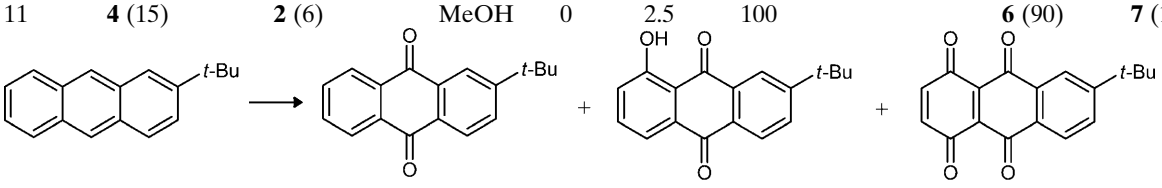
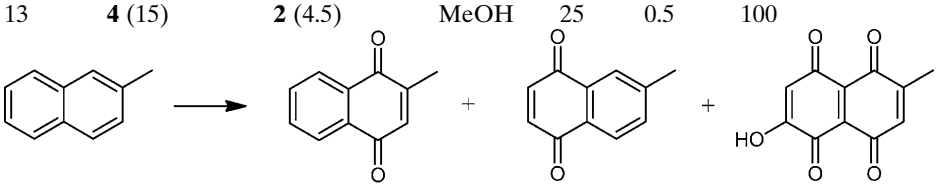
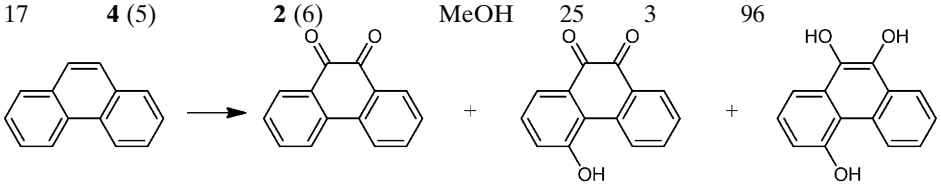
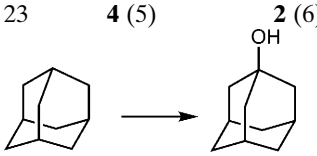
Entry	Catalyst (mol%)	Oxidant (mol equiv)	Solvent	*T* [°C]	Time [h]	Conversion (isolated yield) [%]	Product distribution [%]	
								
	5		6		7			
1	none	**2** (4.5)	MeOH	25	1	1.1	**6** (100)	
2	none	**2** (4.5)	MeOH	25	24	74	**6** (48)	**7** (52)
3	Py (225)	**2** (4.5)	MeOH	25	1	0.5	**6** (100)	
4	Py (225)	**2** (4.5)	MeOH	25	24	25	**6** (59)	**7** (41)
5	Fe^{3+} (100)[a]	**2** (6)	MeOH	25	1	0.4		**7** (100)
6	Fe^{3+} (100)[a]	**2** (6)	MeOH	25	5	2.8		**7** (100)
7	**3** (10)	**1** (7.5)	toluene	25	5	100	**6** (100)	
8	**3** (10)	**2** (7.5)	toluene	25	2[8b]	100	**6** (100)	
9	**4** (10)	**1** (12)	MeOH	25	2	100	**6** (100)	
10	**4** (15)	**2** (6)	MeOH	25	2	100	**6** (85)	**7** (15)
11	**4** (15)	**2** (6)	MeOH	0	2.5	100	**6** (90)	**7** (10)
								
	8		9		10		11	

Table 1. (Continued)

Entry	Catalyst (mol%)	Oxidant (mol equiv)	Solvent	*T* [°C]	Time [h]	Conversion (isolated yield) [%]	Product distribution [%]		
12	**3** (15)	**2** (6)	toluene	25	20[8b]	100 (72)	**9** (100)		
13	**4** (15)	**2** (4.5)	MeOH	25	0.5	100	**9** (76)	**10** (13)	**11** (11)
									
	12		13		14		15		
14	**3** (30)	**2** (6)	toluene	25	24	1.3	**13** (55)	**14** (45)	
15	**4** (15)	**2** (6)	MeOH	25	2	89	**13** (32)	**14** (26)	**15** (42)
16	**4** (30)	**2** (4.5)	MeOH	0	3	87	**13** (39)	**14** (30)	**15** (31)
17	**4** (5)	**2** (6)	MeOH	25	3	96	**13** (33)	**14** (10)	**15** (57)
									
	16		17		18		19		
18	**3** (15)	**2** (6)	toluene	25	2.5	0			
19	**3** (30)	**2** (6)	toluene	25	4	2	**17** (100)		
20	**4** (15)	**2** (6)	MeOH	25	2.5	82 (50.5)	**17** (13)	**18** (66)	**19** (21)
21	**4** (45)	**2** (6)	MeOH	25	3.5	93		**18** (59)	**19** (41)
22	**4** (30)	**2** (6)	MeOH	0	4	44	**17** (40)	**18** (33)	**19** (27)
23	**4** (5)	**2** (6)	MeOH	25	3	100	**17** (11)	**18** (84)	**19** (5)
									
	20		21						
24	**3** (15)	**2** (6)	toluene	25	24	0			
25	**3** (45)	**2** (6)	toluene	25	24	1.8	**21** (100)		
26	**4** (15)	**2** (6)	MeOH	25	24	2.4	**21** (100)		
27	**4** (30)	**2** (6)	MeOH	0	24	0			

[a] Fe(III) acetate was used as a source of the Fe(III) ions.

pervalent oxidants **1** and **2** and catalysts **3** and **4** are presented in Table 1. The use of iodosylbenzene and oxidant **2** in the first reaction in the presence of μ-oxodimer **3** was previously reported in the literature.[8b]

All oxidation reactions were carried out in dry methanol or in toluene using 1.5–2.5 times excess (4.5–7.5 mol equiv of active oxygen per 1 molecule of substrate) with 0.10–0.45 equiv. of the catalyst **3** or **4** or 100–225 equiv. of iron(III) acetate or pyridine in the case of blank experiments (Table 1). After the indicated time, the catalyst was removed by flash chromatography and the obtained solution was analyzed by GC-MS to determine the conversion of aromatic hydrocarbons or adamantane. According to the GC-MS and NMR data, iodobenzene resulting from the reduction of hypervalent iodine reagents and reaction products shown in Table 1 were the only products formed under these reaction conditions. Methanol was found to be the best solvent for the oxidations in the presence of μ-oxodimer **4**, while toluene was used for the reactions catalyzed by μ-oxodimer **3** as previously discussed.[8]

As we have shown earlier,[8b] the oxidation of anthracene with hypervalent iodine reagents **1** and **2** in the absence of catalysts at room temperature in toluene or at 40 °C in dichloromethane proceeds extremely slowly and does not show any measurable conversion to anthraquinone **6** after 24 h. Reagent **2**, however, slowly oxidizes anthracene in methanol at room temperature with a 1% conversion after 1 hour and 74% conversion after 24 h (entries 1 and 2). It should be noted, however, that more reactive oxidant **2** leads to formation of two reaction products after 24 h. The first one is the expected 9,10-anthraquinone **6**, while the second one is 1-hydroxy-9,10-anthraquinone **7**.

The addition of 0.10–0.15 mol equiv of Fe(III)-phthalocyanines **3** and **4** leads to a significant increase in the reaction rate with a 100% conversion reached in 2–5 h for catalyst **3** and 2 h for catalyst **4** at room temperature (entries 7–10). In the case of catalyst **3** and catalyst **4**/oxidant **1** combination (entries 7–9) the only reaction product observed in GC-MS was 9,10-antraquinone, while in the case of catalyst **4**/oxidant **2** combination, 15% of the 1-hydroxy-9,10-antraquinone was observed in the reaction mixture, suggesting that catalyst **4** can further oxygenate a less reactive (as compared to anthracene) 9,10-anthraquinone. Lowering the reaction temperature leads to a slightly slower conversion rate of the reaction in the presence of phthalocyanine **4** but expectedly results in a smaller amount of overoxidized product **7** (entry 11). Since catalysts **3** and **4** degrade during catalytic oxidation reactions, and catalyst **4** has basic pyridine fragments in its core, the oxidation of the anthracene into anthraquinone was tested in the absence of catalysts but in the presence of pyridine (225 equiv.) or Fe(III) salt (100 equiv., entries 3–6). In both cases *inhibition* of the oxidation reaction was clearly observed.

In agreement with our previous reports, the data presented in Table 1 clearly indicate that the oligomeric iodosylbenzene sulfate **2** is the best oxidant, significantly more reactive than the commonly used iodosylbenzene and thus this oxidant was used for the oxidation of the other aromatic compounds presented in Table 1.

The oxidation of the more sterically crowded 2-*tert*-butylanthracene **8** is indicative of the superiority of catalyst **4** (entries 12 and 13). Indeed, with catalyst **3**, 100% conversion of **8** into 2-*tert*-butyl-9,10-anthraquinone can be achieved after 20 h (isolated yield is 72%), while complete oxidation of **8** with catalyst **4** was completed after 30 min. Similar to the oxidation of anthracene, small amounts of two additional overoxidation products **10** and **11** were observed in the reaction mixture (entry 13).

The reasonable oxidation of 2-methylnaphthalene **12** to provitamin K can also be achieved only with the more active catalyst **4** (entries 14–17). Formation of three quinone products **13–15** was observed at 25 and 0 °C. In the reaction at room temperature, the overoxidized quinone **15** is the major reaction product (entries 15 and 17), while lowering the reaction temperature to 0 °C leads to formation of the target quinone **13** as the major reaction product (entry 16).

Catalyst **3** is also not effective in the oxidation of phenanthrene into 5,6-phenanthrenedione **17** at room temperature (entries 18 and 19), while use of catalyst **4** leads to formation of the products **17–19**, which were isolated and characterized by NMR spectroscopy (entries 20–23). Expectedly, longer reaction times for room temperature oxidations favor overoxidation products **18** and **19** (entries 20, 21, 23), while lowering the reaction temperature results in formation of **17** as the major reaction product.

Finally, both catalysts **3** and **4** are not very effective in oxidation of the adamantane into 1-adamantanol (entries 24–27) at 25 and 0 °C.

Conclusions

In summary, the results of our study show that oligomeric iodosylbenzene sulfate **2**/complex **4** combination is an efficient oxygenating pair in the biomimetic catalytic oxidation of aromatic hydrocarbons. New asymmetric μ-oxodimer **4** is a significantly more powerful catalyst as compared to the well-known μ-oxodimer **3** and can catalyze the oxidation of various aromatic substrates.

Experimental Section

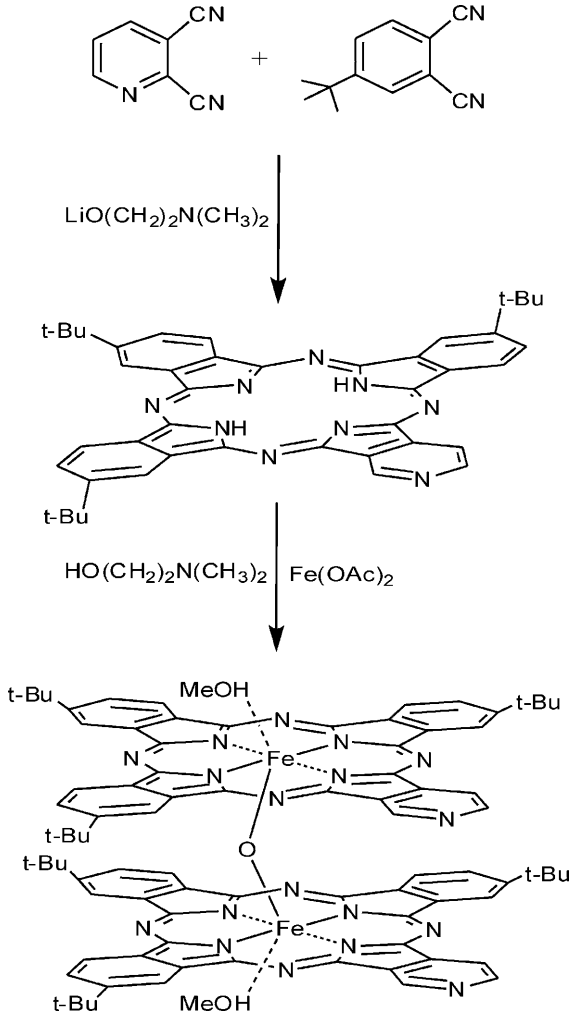
General Methods

All reactions were performed under a dry nitrogen atmosphere with flame-dried glassware. All commercial reagents were ACS reagent grade and used without further purification. Toluene and dichloromethane were distilled from CaH_2 and stored over molecular sieves. Catalyst **3**,[9] iodosylbenzene sulfate **2**[8,10] and iodosylbenzene[2a] were prepared by known methods. GC-MS analysis was carried out with an HP 5890 A Gas Chromatograph using a 5970 Series mass selective detector. The APCI-MS experiment was conducted using a Finnegan LCQ LC-MS system. NMR spectra were recorded on a Varian INOVA instrument with 500 MHz frequency for protons. Chemical shifts are reported in parts per million and referenced to TMS as an internal standard. UV-vis spectra were collected on Jasco V-730 spectrophotomeres. MCD spectra were acquired on OLIS DCM-17 system with 1.4T DeSa permanent magnet.

Preparation of Catalyst 4

The preparation of catalyst **4** is shown in Scheme 1. The asymmetrical metal-free phthalocyanine precursor was synthesized according to the previously reported procedure.[11] Selected data for this compound are: APCI-MS: $m/z = 684$ $[M+1]^+$ 100%; UV-vis ($CHCl_3$): $\lambda = 342$, 605, 634, 659, 685 nm.

The preparation of μ-oxodimer from the asymmetrical metal-free precursor was achieved by the reaction between 0.54 g (0.79 mmol, 1 equiv.) of metal-free phthalocyanine and 1.37 g (7.9 mmol, 10 equiv.) of iron(II) acetate in 5 mL of boiling *N,N*-dimethyl ethanolamine for 8 h under an argon atmosphere. After this period of time, the reaction mixture was poured into water saturated with sodium chloride and the reaction product was filtered. The target complex **4** was purified using basic alumina (Sorbent Technologies, Act. 1, 50–200 μm). First, toluene was used as the eluent to remove reaction impurities and unreacted asymmetrical metal-free phthalocyanine. After this, the target μ-oxodimer **4** was eluted by pure methanol. The methanol was



Scheme 1. Synthetic pathway for preparation of the iron(III) phthalocyanine-(μ-oxodimer) **4**.

evaporated under reduced pressure and the product was finally purified by washing with hexane and recrystallization from methanol/hexane.; yield: 31%; UV-Vis and MCD spectra of **4** are shown in Figure 3, while its APCI-mass spectrum is presented in Figure 4. Selected data for this compound are: UV-Vis (toluene): λ (log ε) = 358 (4.83), 560 sh, 633 sh, 667 sh, 700 nm (4.9); ACPI-MS: $m/z = 1491$ $[M+1]^+$ 100%, 1522 $[M+CH_3OH]^+$ 50%, 1554 $[M+2CH_3OH]^+$. The presence of one or two methanol molecules in **4** was further confirmed by an APCI MS/MS method on the 1554 $[M+2CH_3OH]^+$ peak; IR (KBr): ν = 3068 (Ar-H), 2958 (CH_3), 2925 (CH_3), 2856 (CH_3), 2364, 2345, 1609, 1500, 1482, 1388, 1364, 1327, 1257, 1197, 1082, 1027, 923, 900, 840, 750, 692 cm^{-1}.

Typical Procedure for Catalytic Oxidation of Aromatic Hydrocarbons

A solution of the appropriate hydrocarbon (0.056–0.070 mmol) in toluene or methanol (5–10 mL) was mixed with the amount of the catalyst **3** or **4** shown in Table 1 and the hypervalent iodine oxidant **1** or **2** (4.5–12 equiv. of O),

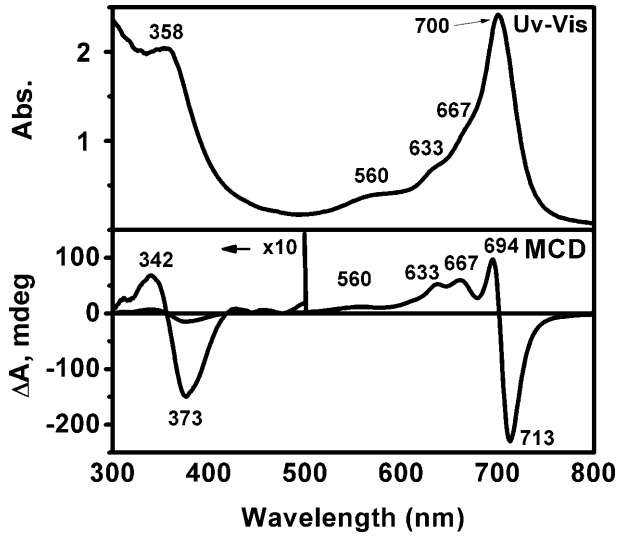


Figure 3. UV-vis (*top*) and MCD (*bottom*) spectra of iron-(III) phthalocyanine-(μ-oxodimer) **4.**

with stirring, at the temperature indicated in Table 1. Samples of the reaction mixture (100 μL) were collected every 30 min, filtered through 2–3 cm of silica gel suspended in a Pasteur pipet, washed with a mixture of ethyl acetate and hexane (2:3 v:v), and then analyzed using GC-MS.

Catalytic Oxidation of Phenantrene

A solution of phenanthrene (25 mg, 0.140 mmol) in methanol (25 mL) was mixed with catalyst **4** (31 mg, 0.02 mmol) and the oxidant **2** (208 mg, 0.281 mmol) at room temperature. The reaction mixture (100 μL samples) was analyzed using GC-MS every 30 min. Upon completion of the reaction, the reaction mixture was concentrated and products were separated using a TLC plate and ethyl acetate/hexane (2:3 v:v) mixture as the eluent. Reaction products were collected as separate fractions and analyzed by GC-MS, ^1H and COSY NMR methods.

Phenanthrene-9,10-dione: Yield: 1.2 mg (4.1%); GC-MS: $m/z = 208$ $(M)^+$; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.21 (d, J = 7.5 Hz, 1.5 Hz, 2H), 8.02 (d, J = 8 Hz, 2H), 7.73 (t, J = 7.5 Hz, 1.5 Hz, 2H), 7.48 (t, J = 8 Hz, 2H).

4-Hydroxyphenanthrene-9,10-dione: Yield: 10.7 mg (34%); GC-MS: $m/z = 224$ $(M)^+$; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.93 (d, J = 7 Hz, 1H), 7.87 (d, J = 5.5 Hz, 2.5 Hz, 2H), 7.79 (d, J = 7.5 Hz, 1.5 Hz, 1H), 7.64 (t, J = 7.5 Hz, 1.5 Hz, 1H), 7.47 (t, J = 8 Hz, 1.5 Hz, 1H), 7.40 (t, J = 7 Hz, 2H).

Phenanthrene-4,9,10-triol: Yield: 3.9 mg (12.3%); GC-MS: $m/z = 226$ $(M)^+$; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.83 (m, 4H), 7.50 (d, J = 7.5 Hz, 1H), 7.3 (m, 2H).

Acknowledgements

This work was supported by a research grant from the National Science Foundation (grant CHE-0702734) and Petrole-

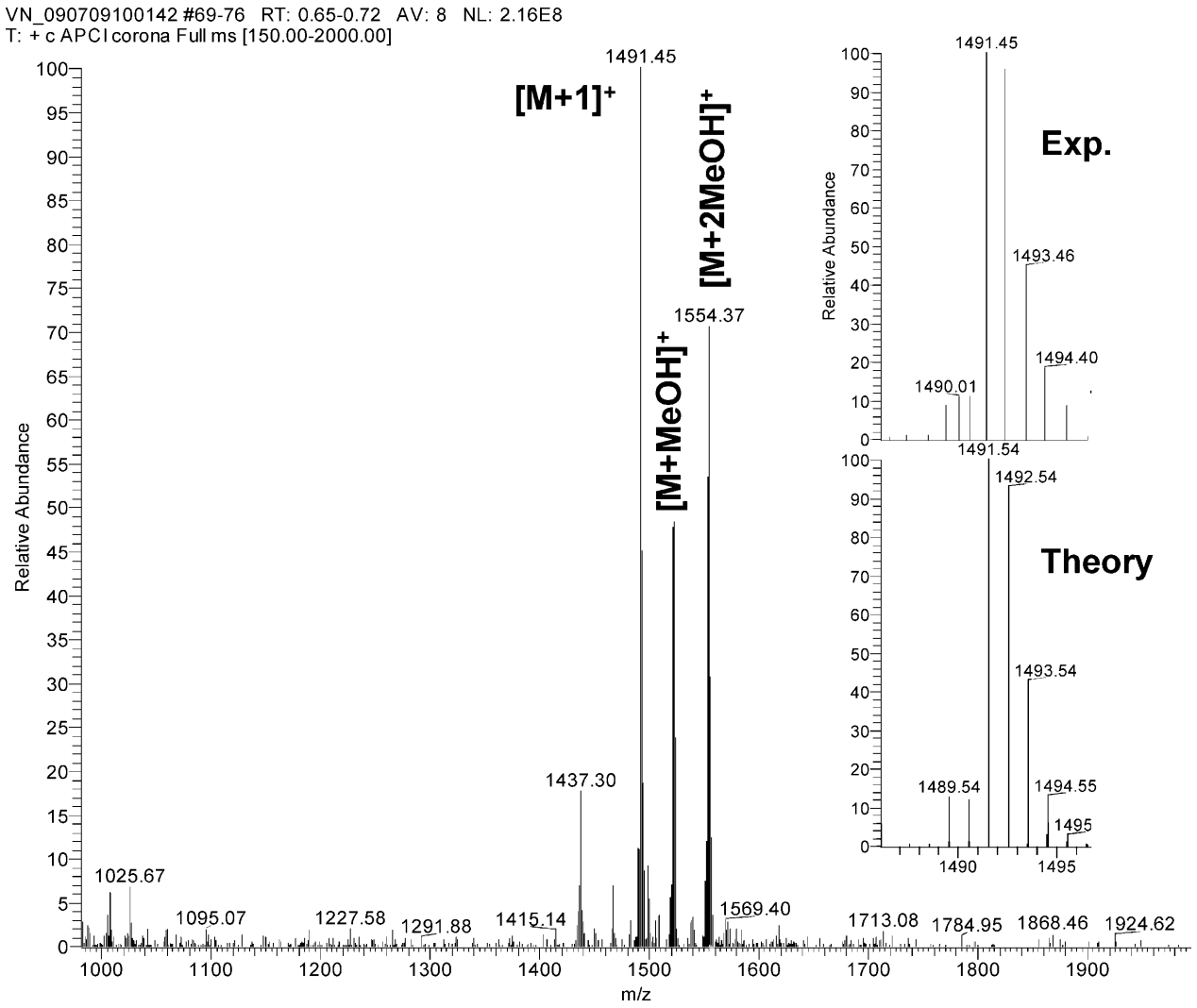


Figure 4. APCI MS of the iron(III) phthalocyanine-(μ-oxodimer) **4**.

um Research Fund, administered by the American Chemical Society (grant PRF-45510-GB-3).

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