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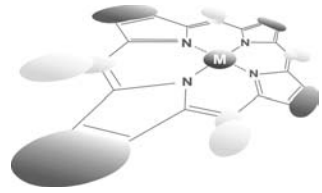

Preparation of N-bridged diiron phthalocyanines bearing bulky or small electron-withdrawing substituents

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ABSTRACT: The synthesis of novel μ-nitrido diiron phthalocyanine with electron-withdrawing substituents is reported: μ-nitrido tetra-methylsulfonylphthalocyanine (**13**), μ-nitrido tetra-ethylsulfonylphthalocyanine (**14**), μ-nitrido tetra-adamantylsulfonylphthalocyanine (**15**), μ-nitrido tetra-cyclohexylsulfonylphthalocyanine (**16**). These complexes were characterized by ESI-MS, UV-vis, FT-IR and EPR techniques. The state of these complexes depends on the size of the substituents. Complexes **13** and **14** bearing small methylsulfonyl and ethylsulfonyl substituents are cationic $(PcFe^{IV}NFe^{IV}Pc)^{+}N_3^{-}$ complexes while complexes **15** and **16** with bulkier adamantylsulfonyl and cyclohexylsulfonyl substituents are formally neutral $PcFe^{III}NFe^{IV}Pc$ complexes which can be represented as PcFe(+3.5)NFe(+3.5)Pc.

KEYWORDS: μ-nitrido dimer, diiron, alkylsulfonyl substituents, catalysis.

INTRODUCTION

Transition metal complexes of phthalocyanines are widely investigated owing to their interesting properties in many areas such as photosensitizers [1, 2], catalysts [1, 3], electrocatalysts [1, 4], sensors [1, 5], nonlinear optical devices [1, 6] and different fields of materials science [1, 7]. These versatile compounds are readily accessible and their properties can be tuned by changing the metal ion as well as by introducing appropriate substituents at the periphery of phthalocyanine ligand. Iron phthalocyanine complexes exhibit good catalytic properties in oxidation [8, 9]. Significantly, the μ-oxo dimer form of iron tetrasulfophthalocyanine supported on silica supports showed better catalytic properties than monomeric one in oxidation of different substrates [10]. In the search for the stable binuclear structures some of us started the study of μ-nitrido diiron macrocyclic complexes with Fe-N-Fe unit and their application in oxidation catalysis [11]. μ-nitrido diiron tetra-*tert*-butylphthalocyanine showed remarkable catalytic properties including mild oxidation of methane [11a] and benzene [11b]. Preparation of μ-nitrido diiron phthalocyanines with electron-withdrawing SO_2R substituents resulted in $Fe^{III}NFe^{IV}$ (R = *t*-Bu) and $Fe^{IV}NFe^{IV}$ (R = *n*-hexyl) complexes showing a promising catalytic activity in the oxidation of alkylaromatic compounds [12]. Thus, binuclear N-bridged iron phthalocyanine complexes emerge as a novel class of oxidation catalysts with interesting catalytic properties. Although a number of N-bridged binuclear complexes on phthalocyanine [13] and porphyrin [14] platforms as well as mixed ligand systems [15] have been described, they often contain unsubstituted macrocyclic ligands. Because of that, these μ-nitrido binuclear complexes exhibit only limited solubility in common organic solvents, preventing their investigation and application in catalysis. Introduction of the substituents on the periphery of phthalocyanine ligand should provide better solubility. In addition, one can influence the catalytic properties by

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the appropriate choice of the nature of the substituents (electron-donating *vs.* electron-withdrawing). Besides the catalytic properties, there are a number of other interesting aspects associated with the synthesis and characterization of μ-nitrido complexes of general formula (Pc) M–N-M(Pc), (Pc)M–N-M(P) and (Pc)M–N-M′(P) (P = porphyrinato anion, M and M′ are transition metal ions): (i) reaction mechanisms of formation of formally mixed valence M^{III}-N-M^{IV} or M^{III}-N-M'^{IV} species; (ii) extensive electronic charge redistribution and magnetic coupling occurring for the two metal ions operated by the bridging N atom along the linearly arranged M–N-M moiety; and (iii) high oxidation state for the Fe atoms (>3) and easy access to stable materials containing iron in a high-valent state, *i.e.* Fe(IV) [16, 17]. Consequently, demand for the preparation of novel μ-nitrido diiron complexes with modified properties is high. Herein, we publish the preparation and characterization of four novel μ-nitrido diiron phthalocyanines with SO_2R electron-withdrawing substituents of different size: small groups (methyl and ethyl) and bulky substituents (cyclohexyl and adamantyl). These μ-nitrido diiron phthalocyanine complexes were characterized by ESI-MS as well as UV-vis, FT-IR and EPR techniques.

EXPERIMENTAL

General

All solvents were dried before use as described in reference 18. X-band (9.5 GHz) EPR spectra were recorded at 77 K on a Bruker ESP 300E spectrometer using a standard rectangular (TE102) EPR cavity (Bruker ER4102ST). Microwave power of 1.6 mW and modulation amplitude 1 G were used. Infrared spectra (IR) were recorded on a Bio-Rad FTS 175C FTIR spectrophotometer. UV-visible absorption spectra were obtained using a Shimadzu 2001 UV Pc spectrophotometer. Mass spectra were measured on a Bruker microTOF spectrometer equipped with electronspray ionization (ESI) source and on a MALDI (Matrix Assisted Laser Desorption Ionization) Bruker Microflex LT using 2,5-dihydroxybenzoic acid as the matrix. ^{1}H and ^{13}C NMR spectra were recorded in deuterated chloroform ($CDCl_3$) on a Varian 500 MHz spectrometer. Sodium methanesulfinate and sodium ethanesulfinate were prepared according to literature protocol [19a].

Synthesis

Preparation of 1,2-dicyano-4-methylsulfonylbenzene (3) [19b]**.** A mixture of 1.73 g (0.01 mol) of 4-nitrophthalonitrile and 1.02 g (0.01 mol) sodium methanesulfinate in 50 mL of dimethyl sulfoxide (DMSO) was stirred for 24 h under argon atmosphere at 80 °C. Then, the mixture was poured into 500 mL of ice water. The resulting solid was collected by filtration and washed with water. After drying in vacuum at 50 °C, the crude product was recrystallized from ethanol. Yield: 1.2 g (60%), mp 166 °C. Anal. calcd. for $C_9H_6N_2O_2S$: C, 52.42; H, 2.93; N, 13.58; S, 15.55%. Found: C, 52.20; H, 2.84; N, 13.29; S, 15.70. ^{1}H NMR (500 MHz, $CDCl_3$): δ, ppm 3.1 (s, 3H), 8.1 (d, 1H), 8.3 (d, 1H), 8.4 (s, 1H). ^{13}C NMR (500 MHz, $CDCl_3$): δ, ppm 145.6, 134.9, 132.6, 132.1, 120.8, 117.8, 114.2, 114.0, 44.5. IR (KBr): ν, cm^{-1} 3100, 3026, 2938, 2236, 1591, 1388, 1325, 1152, 965, 764, 645, 534. ESI-MS: *m/z* 207.31 $[M + H]^+$.

Preparation of 1,2-dicyano-4-ethylsulfonylbenzene (4). 1,2-dicyano-4-ethylsulfonylbenzene (**4**) was synthesized and purified as described above for **3**. The amounts of the reagents employed were 4-nitrophthalonitrile (1.73 g, 0.01 mol), sodium ethanesulfinate (1.28 g, 0.01 mol), and dried DMSO (50 mL). Yield: 1.4 g (62%), mp 130 °C. Anal. calcd. for $C_{10}H_8N_2O_2S$: C, 54.53; H, 3.66; N, 12.72; S, 14.56%. Found: C, 54.12; H, 3.72; N, 12.90; S, 14.12. ^{1}H NMR (500 MHz, $CDCl_3$): δ, ppm 1.3 (t, 3H), 3.2 (q, 3H), 8.0 (d, 1H), 8.2 (d, 1H), 8.3 (s, 1H). ^{13}C NMR (500 MHz, $CDCl_3$): δ, ppm 144.2, 134.7, 132.8, 132.6, 120.6, 117.8, 114.3, 114.1, 50.6, 7.2. IR (KBr): ν, cm^{-1} 3103, 3077, 2943, 2239, 1591, 1387, 1314, 1133, 1051, 849, 738, 654, 497. ESI-MS: *m/z* 221.22 $[M + H]^+$.

Preparation of 1,2-dicyano-4-adamantylthiobenzene (5) [19c]**.** 4-nitrophthalonitrile (2.5 g, 14.5 mmol) and adamantanethiol (2.5 g, 14.6 mmol) were dissolved in anhydrous DMSO (10 mL) under argon atmosphere. After stirring for 15 min at room temperature, dry and finely powdered potassium carbonate (6 g, 43.5 mmol) was added portion-wise over 15 min with efficient stirring. The reaction mixture was stirred under argon at room temperature for 24 h. Then, the mixture was poured into 200 mL of ice-water. The resulting solid was collected by filtration and washed with water. After drying in vacuum at 50 °C, the crude product was recrystallized from ethanol. Yield: 3.3 g (81%), mp 144 °C. Anal. calcd. for $C_{18}H_{18}N_2S$: C, 73.43; H, 6.16; N, 9.51; S, 10.89%. Found: C, 73.10; H, 6.30; N, 9.45; S, 10.70. ^{1}H NMR (500 MHz, $CDCl_3$): δ, ppm 1.6–2.2 (m, 15H), 7.7 (d, 1H), 7.8 (d, 1H), 7.9 (s, 1H). ^{13}C NMR (500 MHz, $CDCl_3$): δ, ppm 141.2, 141.0, 140.1, 133.2, 115.9, 115.4, 115.3, 115.2, 50.1, 44.1, 36.2, 30.1. IR (KBr): ν, cm^{-1} 2914, 2881, 2848, 2232, 1580, 1474, 1339, 1103, 1036, 843, 684, 526. ESI-MS: *m/z* 317.25 $[M + Na]^+$.

Preparation of 1,2-dicyano-4-cyclohexylthiobenzene (6). 1,2-dicyano-4-cyclohexylthiobenzene (**6**) was synthesized and purified as described above for **5**. The amounts of the reagents employed were: 4-nitrophthalonitrile (2.5 g, 14.5 mmol), cyclohexylthiol (1.7 g, 14.6 mmol), potassium carbonate (6 g, 43.5 mmol) and dried DMSO (10 mL). Yield: 2.6 g (75%), mp 93 °C. Anal. calcd. for $C_{14}H_{14}N_2S$: C, 69.39; H, 5.82; N, 11.56; S, 13.23%. Found: C, 68.90; H, 5.76; N, 11.89; S, 13.33. ^{1}H NMR (500 MHz, $CDCl_3$): δ, ppm 1.2–2.2 (m, 10H), 3.3 (m, 1H), 7.5(d, 1H), 7.6 (s, 1H), 7.7 (d, 1H). ^{13}C NMR (500 MHz, $CDCl_3$): δ, ppm 140.7, 130.3, 130.1,

130.0, 117.8, 115.8, 115.6, 111.1, 45.6, 32.8, 25.8, 25.6. IR (KBr): ν, cm^{-1} 2860, 2236, 1578, 1470, 1343, 1102, 1090, 837, 760, 524. ESI-MS: *m/z* 265.18 $[M + Na]^+$.

Preparation of 1,2-dicyano-4-adamantylsulfonylbenzene (7). To a solution of 1,2-dicyano-4-adamantylthiobenzene (3 g, 10 mmol) in dry CH_2Cl_2 (50 mL) cooled at 0 °C was slowly added *m*-chloroperbenzoic acid (17.2 g, 100 mmol) in CH_2Cl_2 (500 mL). The mixture was warmed to room temperature and vigorously stirred at this temperature overnight (12 h). A saturated sodium sulfite solution was then added, and the organic phase was extracted with CH_2Cl_2 (3 × 50 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the solid was recrystallized from ethanol to give 2.6 g (79%) of 1,2-dicyano-4-adamantylsulfonylbenzene as a white solid. mp 266 °C. Anal. calcd. for $C_{18}H_{18}N_2O_2S$: C, 66.23; H, 5.56; N, 8.58; S, 9.82%. Found: C, 66.11; H, 5.14; N, 8.09; S, 9.64. ^1H NMR (500 MHz; $CDCl_3$): δ, ppm 1.4–2.2 (m, 15H), 8.0 (d, 1H), 8.1 (d, 1H), 8.2 (s, 1H). ^{13}C NMR (500 MHz; $CDCl_3$): δ, ppm 140.8, 135.3, 134.9, 134.0, 120.4, 117.0, 114.4, 114.3, 62.5, 35.6, 35.1, 28.2. IR (KBr): ν, cm^{-1} 3100, 3033, 2910, 2860, 2232, 1591, 1455, 1390, 1301, 1284, 1185, 1141, 1040, 856, 628, 560. ESI-MS: *m/z* 325.20 $[M - H]^+$.

Preparation of 1,2-dicyano-4-cyclohexylsulfonylbenzene (8). 1,2-dicyano-4-cyclohexylthiobenzene (**8**) was synthesized and purified as described above for **7**. The amounts of the reagents employed were 1,2-dicyano-4-cyclohexylthiobenzene (3 g, 12 mmol), *m*-chloroperbenzoic acid (20.6 g, 120 mmol) and dry CH_2Cl_2 (550 mL). Yield: 73% (2.4 g), mp 161 °C. Anal. calcd. for $C_{14}H_{14}N_2O_2S$: C, 61.29; H, 5.14; N, 10.21; S, 11.69%. Found: C, 61.08; H, 5.70; N, 10.88; S, 11.20. ^1H NMR ($CDCl_3$): δ, ppm 1.0–2.1 (m, 10H), 2.9 (m, 1H), 8.0 (d, 1H), 8.2 (d, 1H), 8.3 (s, 1H). ^{13}C NMR ($CDCl_3$): δ, ppm 142.8, 134.2, 133.7, 133.3, 120.3, 117.2, 114.0, 113.9, 63.7, 25.3, 24.8, 24.7. IR (KBr): ν, cm^{-1} 3073, 3036, 2856, 2237, 1590, 1456, 1313, 1112, 1109, 847, 766, 542, 525. ESI-MS: *m/z* 313.18 $[M + K]^+$.

Preparation of tetra-(methylsulfonyl)phthalocyaninatoiron(II) (9). 3 (1 g, 4.8 mmol) was heated at 130 °C in a mixture of dry *o*-dichlorobenzene-DMF (3:1) under argon for 8 h in the presence of $FeCl_2$ (1.5 mmol). The solvent was removed under reduced pressure. The blue solid was extracted with CH_2Cl_2. **9** was isolated by chromatography on silica gel using a mixture of CH_2Cl_2-EtOH (10:1). Yield: 250 mg, (24%). Anal. calcd. for $C_{36}H_{24}FeN_8O_8S_4$: C, 49.09; H, 2.75; N, 12.72; S, 14.56%. Found: C, 49.28; H, 2.70; N, 12.98; S, 14.20. UV-vis ($CHCl_3$): λ_{max}, nm (log ε) 665 (4.7), 327 (4.6). IR (KBr): ν, cm^{-1} 2926, 1599, 1404, 1300, 1146, 1047, 834, 720, 578, 530. MALDI-MS: *m/z* 880.14 $[M]^+$; calcd. for $C_{36}H_{24}FeN_8O_8S_4$: 880.12.

Preparation of tetra-(ethylsulfonyl) phthalocyaninatoiron(II) (10). Tetra-(ethylsulfonyl)phthalo-cyaninatoiron(II) (**10**) was synthesized and purified as described above for **9**. The amounts of the reagents employed were: 1,2-dicyano-4-ethylsulfonylbenzene (**4**) (1.5 g, 6.8 mmol), dry *o*-dichlorobenzene-DMF (2 mL), $FeCl_2$ (2.2 mmol). Yield: 995 mg (62%). Anal. calcd. for $C_{40}H_{32}FeN_8O_8S_4$: C, 51.28; H, 3.44; N, 11.96; S, 13.69%. Found: C, 51.08; H, 3.37; N, 11.18; S, 12.94. UV-vis ($CHCl_3$): λ_{max}, nm (log ε) 670 (5.1), 606 (4.2), 336 (4.6). IR (KBr): ν, cm^{-1} 2938, 1605, 1455, 1402, 1306, 1143, 1046, 838, 724, 582, 533. MALDI-MS: *m/z* 936.21 $[M]^+$; calcd. for $C_{40}H_{32}FeN_8O_8S_4$: 936.06.

Preparation of tetra-(adamantylsulfonyl)phthalocyaninatoiron(II) (11). Tetra-(adamantylsulfonyl) phthalocyaninatoiron(II) (**11**) was synthesized and purified as described above for **9**. The amounts of the reagents employed were: 1,2-dicyano-4-adamantylsulfonylbenzene (**4**) (1 g, 3.06 mmol), dry *o*-dichlorobenzene-DMF (3 mL), $FeCl_2$ (1.02 mmol). Yield: 495 mg (47%). Anal. calcd. for $C_{72}H_{72}FeN_8O_8S_4$: C, 63.52; H, 5.33; N, 8.23; S, 9.42%. Found: C, 63.21; H, 5.67; N, 8.16; S, 9.88. UV-vis ($CHCl_3$): λ_{max}, nm (log ε) 683 (4.8), 336 (4.5). IR (KBr): ν, cm^{-1} 2925, 2848, 1602, 1513, 1404, 1300, 1140, 1090, 1037, 970, 826, 750, 704, 580, 554. MALDI-MS: *m/z* 1361.54 $[M + H]^+$; calcd. for $C_{72}H_{72}FeN_8O_8S_4$: 1360.37.

Preparation of tetra-(cyclohexylsulfonyl)phthalocyaninatoiron(II) (12). Tetra-(cyclohexylsulfonyl) phthalocyaninatoiron(II) (**12**) was synthesized and purified as described above for **9**. The amounts of the reagents employed were: 1,2-dicyano-4-cyclohexylsulfonylbenzene (**4**) (1 g, 3.65 mmol), dry *o*-dichlorobenzene-DMF (3 mL), $FeCl_2$ (1.12 mmol). Yield: 420 mg (40%). Anal. calcd. for $C_{56}H_{56}FeN_8O_8S_4$: C, 58.32; H, 4.89; N, 9.72; S, 11.12%. Found: C, 58.06; H, 4.37; N, 9.95; S, 10.88. UV-vis ($CHCl_3$): λ_{max}, nm (log ε) 681 (4.7), 326 (4.3). IR (KBr): ν, cm^{-1} 2938, 2856, 1605, 1449, 1402, 1306, 1145, 1102, 1050, 1002, 889, 824, 758, 683, 591, 548. MALDI-MS: *m/z* 1152.77 $[M]^+$; calcd. for $C_{56}H_{56}FeN_8O_8S_4$: 1152.25.

μ-nitrido-bis[tetra-(methylsulfonyl)phthalocyaninatoiron] (13). 9 (170 mg, 0.19 mmol) and sodium azide (1.1 g) were suspended in α-chloronaphthalene (70 mL) under argon. The mixture was heated for 24 h at 190 °C under intensive stirring. The reaction mixture was cooled and resulting dark blue solution was filtered. The dark blue solid was washed with water and ethanol. The solution was chromatographed on Al_2O_3 (neutral) with CH_2Cl_2 to remove impurities. Then, **13** was collected using CH_2Cl_2:EtOH (1:1) as eluent. Evaporation of solvent afforded pure **13** as a dark blue powder. Yield: 100 mg (59%). IR (KBr): ν, cm^{-1} 928 (Fe=N-Fe). UV-vis ($CHCl_3$): λ_{max}, nm (log ε) 654 (4.3), 319 (4.5). ESI-MS: *m/z* 1797.04 $[M + Na]^+$; calcd. for $C_{72}H_{48}Fe_2N_{17}O_{16}S_8Na$: 1796.98.

μ-nitrido-bis[tetra-(ethylsulfonyl)phthalocyaninatoiron] (14). μ-nitrido-bis [tetra-(ethylsulfonyl)phthalocyaninatoiron] (**14**) was synthesized and purified as described above for **13**. The amounts of the reagents employed were: tetra-(ethylsulfonyl)phthalocyaninatoiron(II) (**10**) (170 mg, 0.18 mmol), α-chloronaphthalene, NaN_3 (1.1 g). Yield: 110 mg (64%). IR (KBr): ν, cm^{-1} 930 (Fe=N-Fe). UV-vis ($CHCl_3$): λ_{max}, nm (log ε) 652 (4.3), 319 (4.5). ESI-MS: *m/z* 1909.36 $[M + Na]^+$; calcd. for $C_{80}H_{64}Fe_2N_{17}O_{16}S_8Na$: 1909.11.

μ-nitrido-bis[tetra-(adamantylsulfonyl)phthalocyaninatoiron] (15). 11 (200 mg, 0.147 mmol) and sodium azide (1.5 g) were suspended in xylenes (70 mL) under argon. The mixture was heated for 24 h at 150 °C under intensive stirring. The reaction mixture was cooled and resulting dark blue solution was separated from insoluble material by filtration. The solution was chromatographed on Al_2O_3 (neutral) with CH_2Cl_2 to remove impurities. Then, **15** was collected using CH_2Cl_2:EtOH (100:1) mixture as eluent. Evaporation of solvent afforded pure **15** as a dark blue powder. Yield: 100 mg (50%). IR (KBr): ν, cm^{-1} 930 (Fe=N-Fe). UV-vis ($CHCl_3$): λ_{max}, nm (log ε) 639 (5.09), 319 (4.2). ESI-MS: *m/z* 2760.03 $[M + Na]^+$; calcd. for $C_{144}H_{144}Fe_2N_{17}O_{16}S_8Na$: 2759.74.

μ-nitrido-bis[tetra-(cyclohexylsulfonyl)phthalocyaninatoiron] (16). 12 (100 mg, 0.086 mmol) and sodium azide (1.5 g) were suspended in dry dimethylsulfoxide (70 mL) under argon. The mixture was heated for 24 h at 170 °C under intensive stirring. The reaction mixture was cooled and resulting dark blue solution was separated from insoluble material by filtration. The solution was chromatographed on Al_2O_3 (neutral) with CH_2Cl_2 to remove impurities. Then, **16** was collected using CH_2Cl_2:EtOH (100:1) mixture as eluent. Evaporation of solvent afforded pure **16** as a dark blue powder. Yield: 48 mg (48%). IR (KBr): ν, cm^{-1} 931 (Fe=N-Fe). UV-vis ($CHCl_3$): λ_{max}, nm (log ε) 634 (4.3), 319 (4.5). ESI-MS: *m/z* 2341.43 $[M + Na]^+$; calcd. for $C_{112}H_{112}Fe_2N_{17}O_{16}S_8Na$: 2341.48.

Reduction of μ-nitrido dimers 13 and 14. $[FePc(SO_2methyl)_4]_2N$ (**13**) or $[FePc(SO_2ethyl)_4]_2N$ (**14**) (25 mg) was dissolved in CH_2Cl_2 and hydrazine (1 mL) was added. This mixture was constantly stirred for 2 h under argon. After evaporation of all the components, the crude product was dissolved in CH_2Cl_2 and the solution was chromatographed on Al_2O_3 (neutral) with CH_2Cl_2:EtOH (100:1) mixture. The product was recovered by evaporation of the solvent.

Oxidation of μ-nitrido dimers 15 and 16. $[FePc(SO_2adamantyl)_4]_2N$ (**15**) or $[FePc(SO_2cyclohexyl)_4]_2N$ (**16**) (25 mg) was dissolved in CH_2Cl_2 and 1.0 g of oxidant ($H_5PV_2Mo_{10}O_{40}$) was added. This mixture was constantly stirred for 2 h under argon. The reaction mixture was then filtered and the solution was chromatographed on Al_2O_3 (neutral) with CH_2Cl_2:EtOH (100:1) mixture. The product was recovered by evaporation of the solvent.

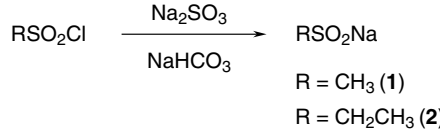
RESULTS AND DISCUSSION

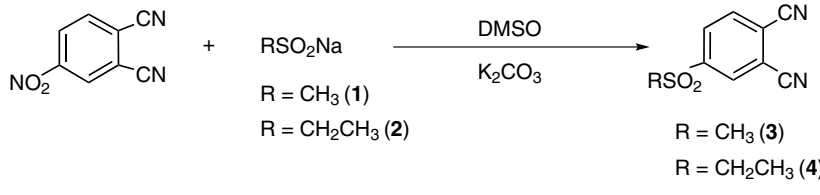
Synthesis and characterization of the monomers

The synthesis of alkylsulfonyl phthalonitriles is commonly carried out by oxidation of alkylthio-substituted phthalonitrile with oxidant such as *m*-chloroperbenzoic acid (m-CPBA) or hydrogen peroxide (H_2O_2) [20]. However, methyl and ethyl sulfonyl phthalonitriles are difficult to prepare from corresponding thiols because of their gaseous state. To overcome this problem, we used sodium methanesulfinate and sodium ethanesulfinate to obtain alkylsulfonyl phthalonitriles directly, thus avoiding an oxidation step (Scheme 1). Sodium alkylsulfinate salts can easily be prepared from corresponding RSO_2Cl by treament with Na_2SO_3 in high 92% yield [19]. This approach afforded methyl (**3**) and ethyl (**4**) sulfonyl-substituted phthalonitriles with 60 and 62% yield, respectively.

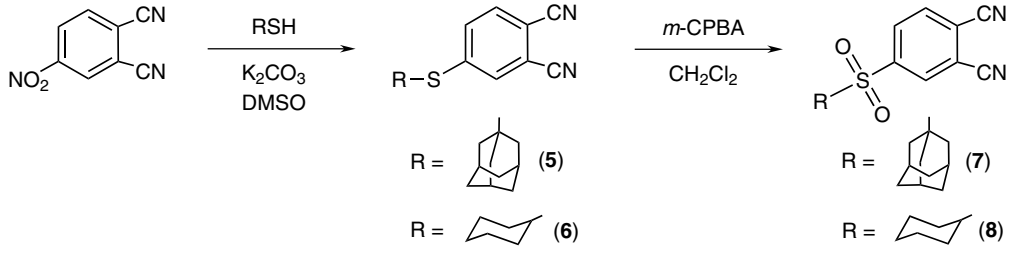
ESI-MS spectra indicated the formation of **3** and **4**. IR spectra of **3** and **4** show the typical C≡N stretching vibration at 2236 and 2239 cm^{-1}. O=S=O vibrations around 1130 and 1320 cm^{-1} confirmed the alkylsulfonyl substitution. The intense peaks at 1152 and 1325 cm^{-1} (**3**) and at 1133 and 1314 cm^{-1} (**4**) were assigned to O=S=O stretching vibrations of alkylsulfonyl group.

Phthalonitriles **7** and **8** were synthesized in two steps (Scheme 2).

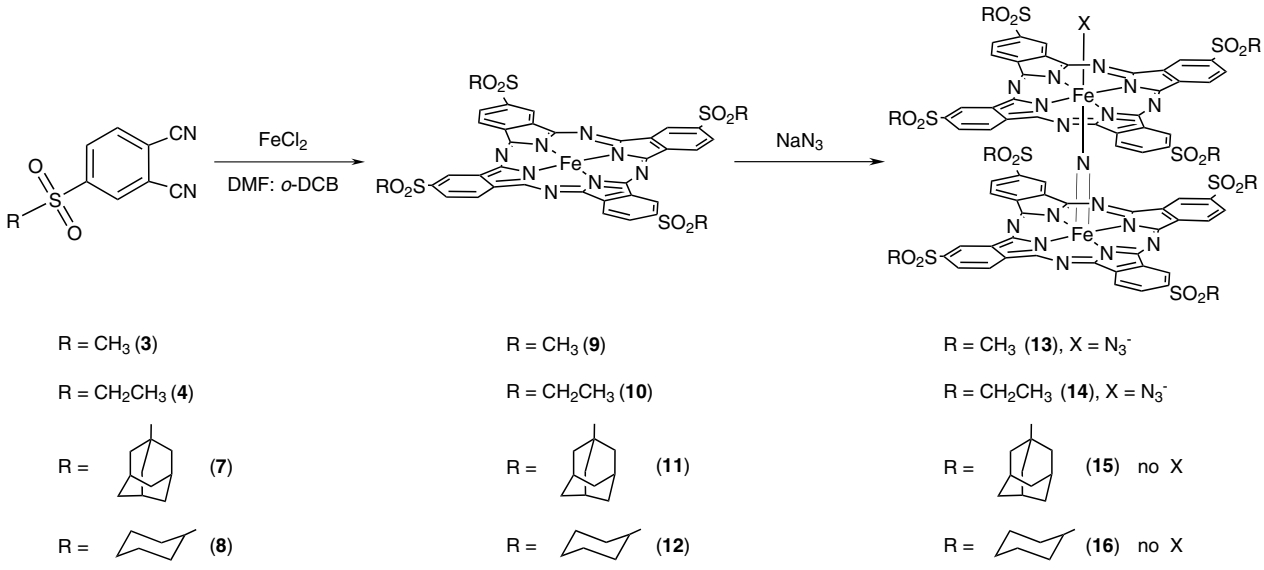




Scheme 1. Synthesis of alkylsulfonyl-substituted phthalonitriles using sodium akylsulfinate salts



Scheme 2. Synthesis of alkylsulfonyl-substituted phthalonitriles from alkylthio phthalonitriles



Scheme 3. Synthesis of alkylsulfonyl-substituted μ-nitrido diiron phthalocyanines

The treatment of 4-nitrophthalonitrile with corresponding thiols and K_2CO_3 in DMSO afforded the thioethers **5** and **6** with 81% and 75% yield, respectively. Their oxidation with *m*-chloroperbenzoic acid in CH_2Cl_2 gave alkylsulfonyl phthalonitriles **7** and **8** in good yields, 79% and 73%, respectively. The IR spectra of **5**, **6**, **7** and **8** show the typical C≡N stretching vibration at 2232, 2236, 2232 and 2237 cm^{-1}. ^1H NMR spectra of alkylsulfonylphthalonitriles are different from those of alkylthiophthalonitriles. While the aromatic protons of alkylthiophthalonitriles appear at 7.5–7.8 ppm, the aromatic protons of alkylsulfonylphthalonitriles shifted at 8.0–8.3 ppm, reflecting the increase of electron-withdrawing character of substituents upon oxidation to SO_2R.

The syntheses of iron phthalocyanines **9**, **10**, **11** and **12** were achieved by treating the corresponding phthalonitriles (**3**, **4**, **7** and **8**) with $FeCl_2$ in the *o*-dichlorobenzene-DMF (3:1) mixture at reflux temperature (Scheme 3).

The *o*-dichlorobenzene-DMF mixture was used for these preparations since dimethylaminoethanol could not be used because of the decomposition of the alkylsulfonylphthalonitriles under the reaction conditions [20]. The sharp peak of C≡N vibrations in the IR spectra of phthalonitriles **3**, **4**, **7** and **8** at 2236, 2239, 2233 and 2237 cm^{-1}, respectively, disappeared after conversion into iron phthalocyanines. After purification by column chromatography alkylsulfonyl-substituted iron phthalocyanines were characterized by UV-vis, IR and MS techniques. UV-vis spectra showed expected Q and B phthalocyanine bands. Interestingly, Q band maxima of methyl (**9**), ethyl (**10**), cyclohexyl (**12**) and adamantyl (**11**) substituted phthalocyanines were observed at 665, 670, 681 and 683 nm, respectively. The reason for this red shift of Q band with increase of bulkiness of substituents is not yet clear. The IR spectra of all the alkylsulfonyl-substituted iron phthalocyanines clearly indicates the presence of sulfonyl function (O=S=O). The intense peaks at 1159 and 1310 cm^{-1} (**9**), at 1145 and 1305 cm^{-1} (**10**), at 1150 and 1300 cm^{-1} (**11**) and at 1146 and 1305 cm^{-1} (**12**) were assigned to the O=S=O stretching vibrations of alkylsulfonyl group. The peaks at 2925 and 2860 cm^{-1} (**9**), at 2938 and 2878 cm^{-1} (**10**), at 2908 and 2849 cm^{-1} (**11**) and at 2934 and 2860 cm^{-1} (**12**) were assigned to C-H stretching vibrations. The observation of C-H stretching vibrations in the range of 2940–2850 cm^{-1} and O=S=O vibrations around 1160 and 1300 cm^{-1} confirmed the retention of alkylsulfonyl substituents in phthalocyanines **9**, **10**, **11** and **12**. MALDI-MS spectra showed expected molecular peaks of **9**, **10**, **11** and **12**. $[M]^+$ peak was observed at $m/z = 880$ for **9**, at $m/z = 936$ for **10** and $[M + H]^+$ peak was observed at $m/z = 1361$ for **11**, $[M]^+$ peak was observed at $m/z = 1152$ for **12**.

Synthesis and characterization of the μ-nitrido dimers

μ-nitrido diiron phthalocyanines are usually prepared by treatment of monomeric iron complex with NaN_3 at high temperature in chloronaphthalene [15]. These complexes can also be prepared using xylene as solvent [11, 12]. The choice of solvent depends on the solubility of monomer precursor. μ-nitrido dimeric complexes **13** and **14** were obtained by treatment of **9** and **10** with NaN_3 in refluxing α-chloronaphthalene with yields of 59% and 64%, respectively. Complex **15** was prepared by treatment of **11** with NaN_3 in refluxing xylene in 50% yield. Since the monomeric complex **12** was not soluble in xylene, the μ-nitrido dimer **16** was prepared in refluxing DMSO in 48% yield.

The successful preparation of **13**, **14**, **15** and **16** was evidenced by ESI-MS analyses, FT-IR, UV-vis and EPR methods.

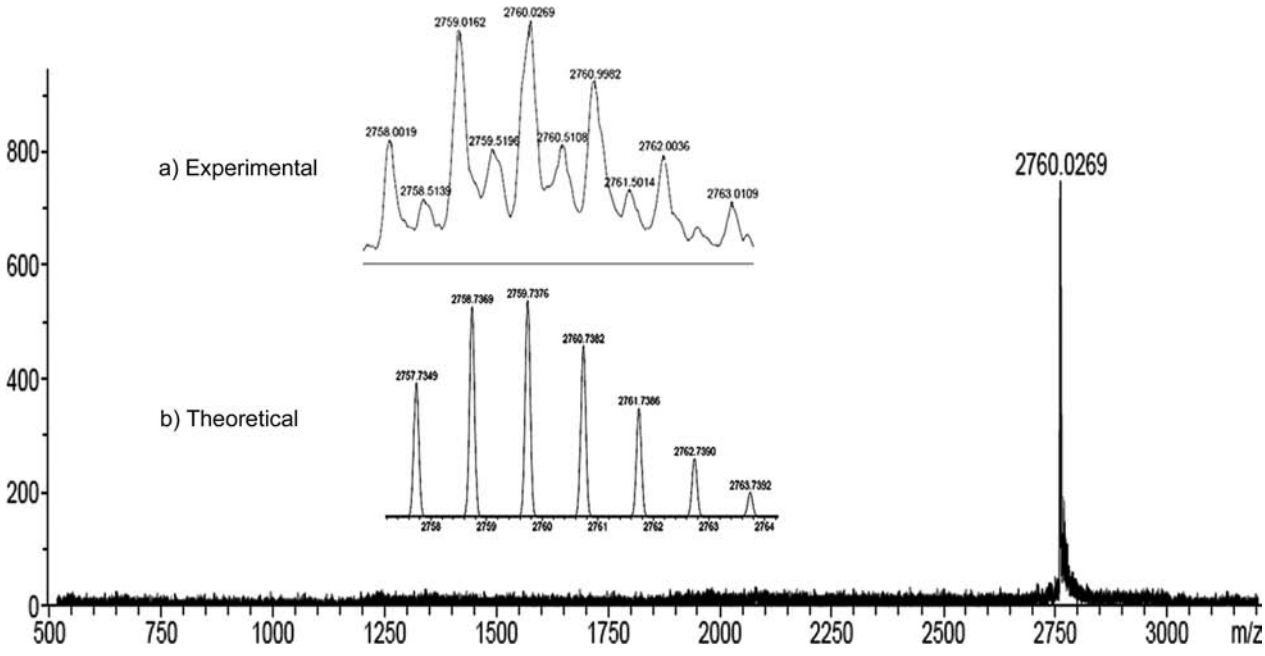


Fig. 1. Molecular peak cluster of **15** in ESI-MS spectrum (a) and simulated molecular peak cluster for **15**, $C_{144}H_{144}Fe_2N_{17}O_{16}S_8Na$ (b)

The ESI-MS spectra of the four μ-nitrido complexes exhibit unique molecular peaks corresponding to the expected values of the molecular ion with sodium: *m/z* = 1797.04 $[M + Na]^+$ for **13**, *m/z* = 1911.36 $[M + Na]^+$ for **14**, *m/z* = 2760.03 $[M + Na]^+$ for **15** and *m/z* = 2341.43 $[M + Na]^+$ for **16**. The isotopic patterns fit the theoritical ones (see the spectrum of the adamantyl derivative (**15**) on Fig. 1), confirming the proposed structures.

The IR spectrum of unsubstituted μ-nitrido diiron phthalocyanine $(PcFe)_2N$ exhibit characteristic absorptions due to the anti-symmetric Fe-N=Fe stretching vibration at 915 cm^{-1} [13a]. This Fe-N=Fe vibration is red-shifted to about 930 cm^{-1} for substituted derivatives, similar to the previously described *tert*-butyl, *tert*-butylsulfonyl and hexylsulfonyl substituted derivatives (signals respectively shifted to 938 cm^{-1} [11], 931 and 929 cm^{-1} [12]). Accordingly, the Fe-N-Fe anti-symmetric stretching vibrations in the IR spectra of **13**, **14**, **15** and **16** are clearly seen at 928, 930, 930 and 931 cm^{-1}, respectively (Fig. 2).

The four prepared μ-nitrido complexes **13**, **14**, **15** and **16** can be divided into two groups depending on the size of their substituents: **13** and **14** bear small substituents (methyl and ethyl), whereas **15** and **16** have bulky substituents (adamantyl and cyclohexyl groups, respectively). The two dimers with small substituents (**13** and **14**) have nearly identical IR spectra (Fig. 2A,B), demonstrating that both their oxidation state and their geometry are similar. In contrast, despite their same oxidation state, the IR spectra of the two dimers bearing bulky substituents (**15** and **16**) are different (Fig. 2C,D). This is probably due to a different geometric arrangement modifying the recorded vibrations, the steric hindrance of an adamantyl group being more important than the one of a cyclohexyl group, thus imposing maybe more rigid structures even if adamantyl and cyclohexyl substituents can both be considered as being bulky.

The IR spectra of **13** and **14** having small substituents (Me and Et) showed a strong signal at 2030 and 2034 cm^{-1}, respectively, assigned to N_3^- vibration (Fig. 3) while the signal in this range was absent in the spectra of **15** and **16** with bulky substituents. These data suggest the presence of an azide anion needed to compensate a positive charge of **13** and **14**. Thus, **13** and **14** can be tentatively assigned as $(PcFe^{IV}NFe^{IV}Pc)^+N_3^-$ complexes. The absence of N_3^- signal in IR spectra of **15** and **16** suggests that **15** and **16** are neutral: this is consistent with $PcFe^{III}NFe^{IV}Pc$ structure. In addition, the complexes bearing small substituents exhibit peaks of strong intensity around 960 cm^{-1} that are not observable on the spectra of **15** and **16**. This may be due to the different oxidation state of the complexes.

The solid-state EPR spectra of the four N-bridged dimers were recorded at 77 K. $[FePc(SO_2methyl)_4]_2N$ (**13**) and $[FePc(SO_2ethyl)_4]_2N$ (**14**) show no EPR signals confirming Fe(IV)Fe(IV) formulation. $[FePc(SO_2adamantyl)_4]_2N$ (**15**) and $[FePc(SO_2cyclohexyl)_4]_2N$ (**16**) dimers show a typically axially symmetry spectrum (g = 2.101, g = 2.109), consistent with a low-spin complex having an A_1 ground state (Fig. 4). These parameters are similar to those observed for non-substituted nitrido-dimers of Fe(III) octaphenyltetraazaporphine and appear to be indicative of extensive delocalization over the two iron centers. The absence of nitrogen hyperfine structure in EPR spectrum is in accordance with $Fe^{+3.5}$–N^{-3}–$Fe^{+3.5}$ formalism [14c]. μ-nitrido bridged species exhibit an exceptional inertness and stability because of the delocalization of an unpaired electron. Data obtained by other spectroscopic methods

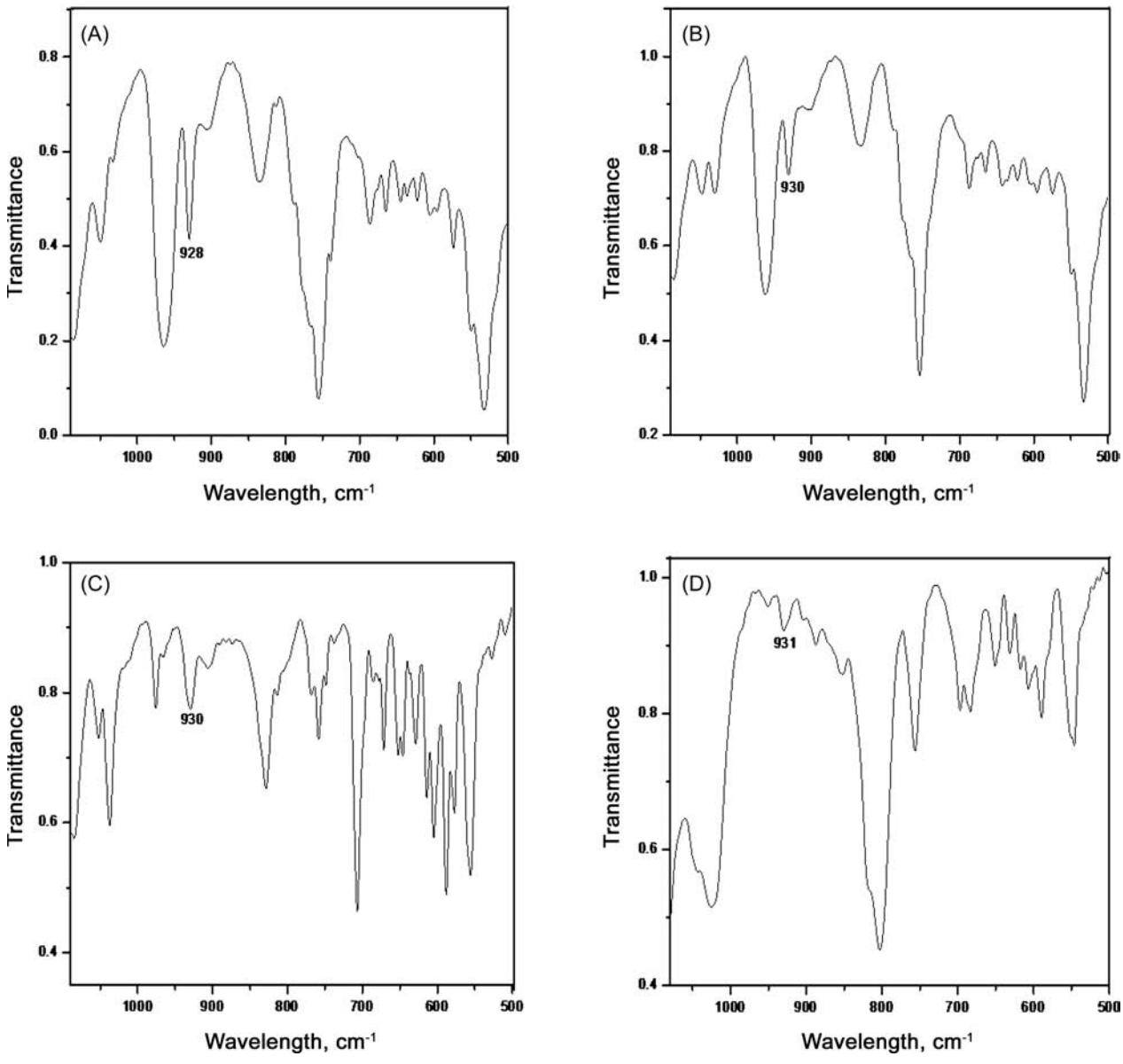


Fig. 2. IR spectra of $[FePc(SO_2methyl)_4]_2N$ (**13**) (**A**), $[FePc(SO_2ethyl)_4]_2N$ (**14**) (**B**), $[FePc(SO_2adamantyl)_4]_2N$ (**15**) (**C**) and $[FePc(SO_2cyclohexyl)_4]_2N$ (**16**) (**D**)

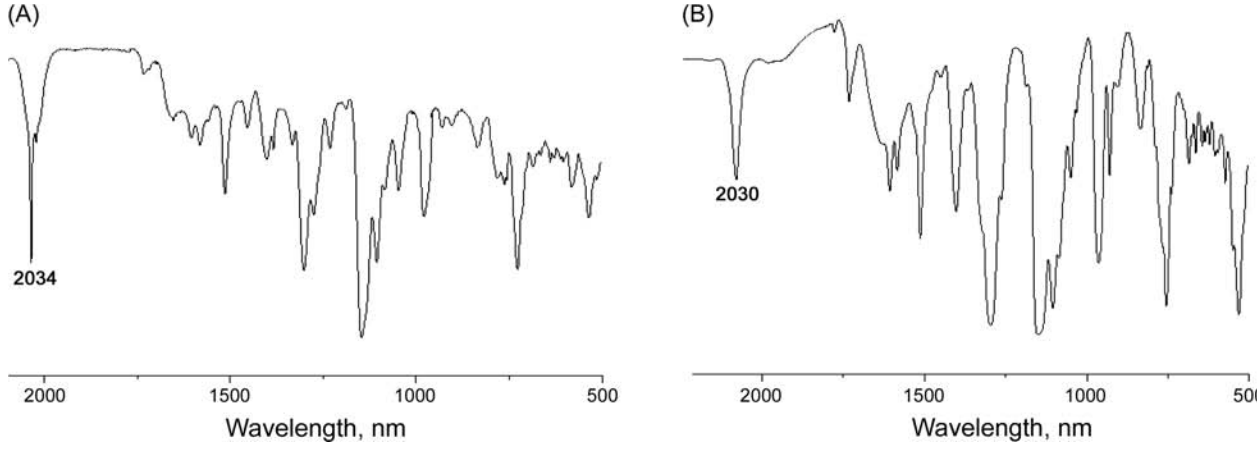


Fig. 3. Expansion of IR spectra of **13** $[FePc(SO_2methyl)_4]_2N$ (**A**) and **14** $[FePc(SO_2ethyl)_4]_2N$ (**B**)

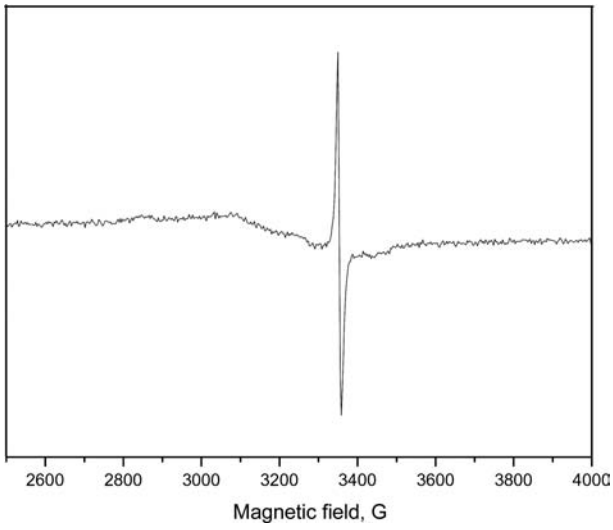


Fig. 4. X band 77 K EPR spectrum of $[FePc(SO_2adamantyl)_4]_2N$ dimer (**15**)

Table 1. Q band values of phthalocyanine monomer, neutral and oxidized cationic dimers

	Q band values (λ, nm)			
Substituent	methyl	ethyl	adamantyl	cyclohexyl
Monomer	665	670	683	681
Neutral dimer	—	—	639	634
Oxidized cationic dimer	654	652	651	649

are also in agreement with formulation of **15** with adamantylsulfonyl and **16** with cyclohexylsulfonyl substituents as neutral $Fe^{III}Fe^{IV}$ N-bridged dimer and **13** with methylsulfonyl and **14** with ethylsulfonyl as cationic $Fe^{IV}Fe^{IV}$ complex containing N_3^- for compensation of charge. The presence of N_3^- in **13** and **14** were evidenced by the presence of 2034 and 2030 cm^{-1} strong signal in IR spectrum.

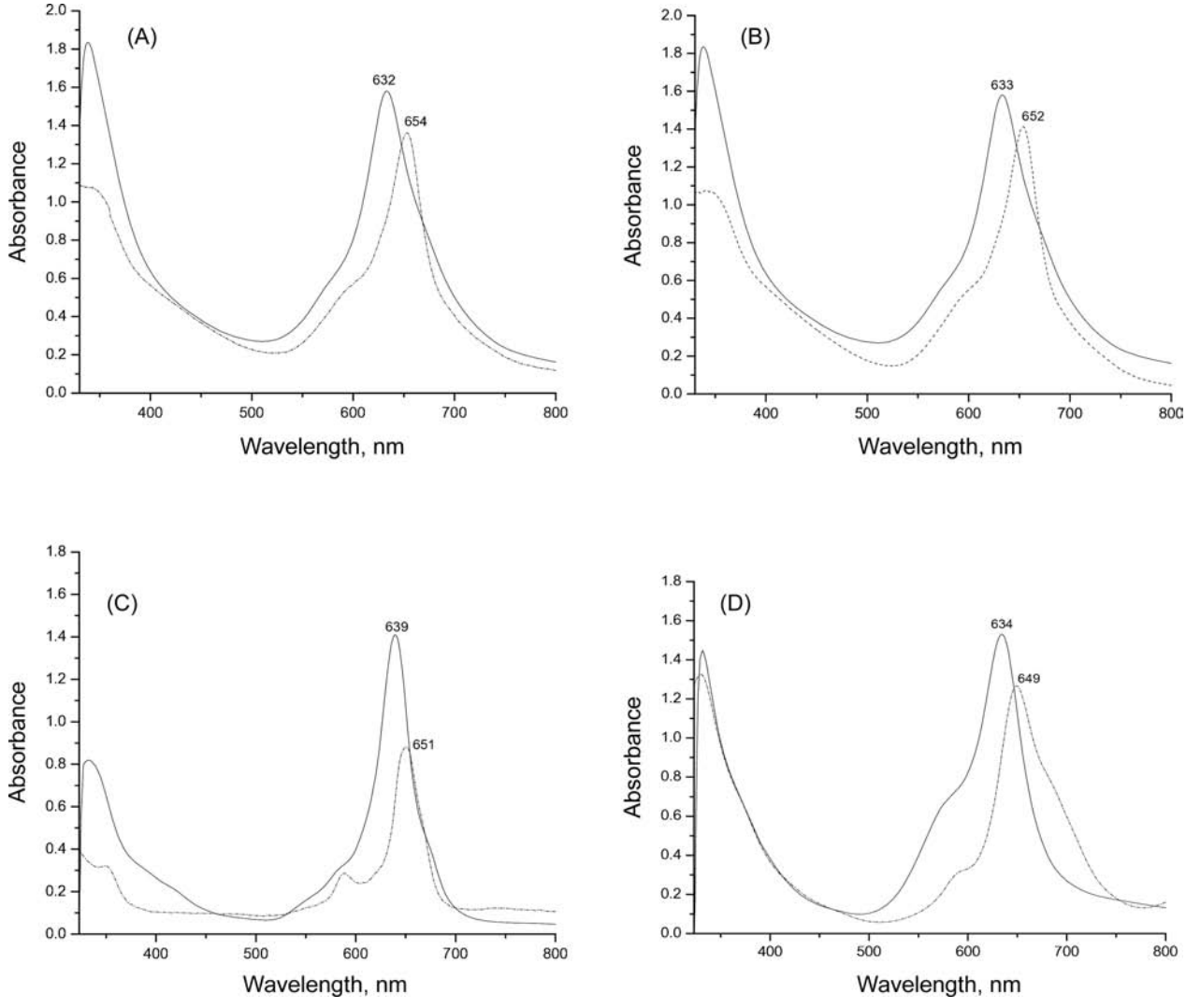


Fig. 5. UV-vis spectra of **13** (dash line) and reduced **13** (solid line) (A), **14** (dash line) and reduced **14** (solid line) (B), **15** (solid line) and oxidized **15** (dash line) (C), **16** (solid line) and oxidized **16** (dash line) (D). Oxidation and reduction experiments were performed using $H_5PV_2Mo_{10}O_{40}$ and hydrazine, respectively, in CH_2Cl_2 under argon as described in the Experimental section

Phthalocyanine systems exhibit two strong absorption bands in electronic absorption spectra. The positions of Soret band (near 340 nm) and of intense Q band (between 600 and 700 nm due to π–π* ligand transition) of phthalocyanine complexes are affected by electronic interaction between ligands as well as by the state of central atom, axial ligation and peripheral substitution [21, 22]. The UV-vis spectra of **13**, **14**, **15** and **16** have been recorded: the strong π–π interaction between two phthalocyanine moieties in dimers results in a blue shift as compared with monomer complexes: from 665 nm to 654 nm for **9/13**, from 670 nm to 652 nm for **10/14**, from 683 nm to 639 nm for **11/15** and from 681 nm to 634 nm for **12/16**, respectively (Table 1).

Q bands of oxidized **13** and **14** ($Fe^{IV}Fe^{IV}$ state) are red-shifted compared to those of neutral **15** and **16** ($Fe^{III}Fe^{IV}$ state). This difference can be explained by the difference in the oxidation state of iron: it has been previously described that unsubstituted neutral $(FePc)_2N$ can easily be oxidized to cationic $(FePc)_2N^+$ complex, resulting in a red shift of Q band from 626 nm to 634 nm in pyridine [13a].

Thus, **15** and **16**, obtained as $PcFe^{IV}NFe^{III}Pc$ neutral form, were oxidized by $H_5PV_2Mo_{10}O_{40}$ to $PcFe^{IV}NFe^{IV}Pc^+$. In turn, **13** and **14**, synthesized as $PcFe^{IV}NFe^{IV}Pc^+$ cationic oxidized form, were reduced by hydrazine. Figure 5 shows the UV-vis spectra of the dimers in their two oxidation states. These experiments indicate interconversion between $Fe^{III}Fe^{IV}$ and $Fe^{IV}Fe^{IV}$ states and confirm formulations of **13**, **14**, **15**, **16** based on IR and EPR data.

CONCLUSION

We have prepared four novel N-bridged diiron phthalocyanine complexes bearing small and bulky electron-withdrawing alkylsulfonyl (alkyl = methyl, ethyl, cyclohexyl and adamantyl) substituents which were characterized by ESI-MS, UV-visible, FT-IR and EPR spectroscopies. Complexes **13** and **14** bearing methylsulfonyl and ethylsulfonyl substituents are cationic $(PcFe^{IV}NFe^{IV}Pc)^+N_3^-$ complexes while complexes **15** and **16** with bulkier adamantylsulfonyl and cyclohexylsulfonyl substituents are formally neutral $PcFe^{III}NFe^{IV}Pc$ complexes. Due to rapid electron exchange **15** and **16** can be described as $Fe^{3.5}$–N–$Fe^{3.5}$ system with two equivalent Fe(+3.5) sites as proposed by Ercolani *et al.* in the case of the unsubstituted complex [13]. The influence of alkylsulfonyl substituents on the oxidation state of N-bridged diiron complexes is striking, taking into account their very close electron-withdrawing properties. The size of alkyl substituents is clearly important. One can suggest that geometrical conformations of dimers could not be the same in the case of small and bulky alkylsulfonyl substituents. Depending on the sterical factors, the distances between two phthalocyanine planes and/or staggering angle between them could be different in two cases, thus influencing the ground oxidation state. In order to get insight further spectroscopic and theoretical studies are necessary. X-ray structural determination would be especially useful, but in the case of tetra-substituted phthalocyanines this is highly challenging because of the presence of four positional isomers. It is worth noting that an N-bridged diiron tetra-substituted phthalocyanine contains ten positional isomers. Taking into account the remarkable catalytic properties of this kind of complexes [11, 12], potential applications of these N-bridged diiron complexes as catalysts in oxidation will be studied further.

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