Journal of Fluorine Chemistry 142 (2012) 60–66

Contents lists available at SciVerse ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Synthesis and characterization of novel fluoroether-substituted phthalocyanines

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ARTICLE INFO

Article history:
Received 30 March 2012
Received in revised form 18 June 2012
Accepted 19 June 2012
Available online 28 June 2012

Keywords:
Phthalocyanine
Fluoroether
^{19}F NMR
^{19}F COSY

ABSTRACT

The synthesis of 1H,1H-nonafluoro-3,6-dioxaheptan-1-ol with 4-nitrophthalonitrile and 4,5-dichlorophthalonitrile in the presence of K_2CO_3 leads to the formation of 4-{2,2-difluoro-2-[1,1,2,2-tetrafluoro-2-(trifluoromethoxy)ethoxy]ethoxy}phthalonitrile (**1**), 4-chloro-5-{2,2-difluoro-2-[1,1,2,2-tetrafluoro-2-(trifluoromethoxy)ethoxy] ethoxy}-phthalonitrile (**2**), and 4,5-bis{2,2-difluoro-2-[1,1,2,2-tetrafluoro-2-(trifluoromethoxy)ethoxy]ethoxy}phthalonitrile (**3**), respectively. Metal free phthalocyanines were synthesized by tetramerization of the phthalonitriles in 2-(dimethylamino)ethanol while metallophthalocyanines were prepared in the presence of zinc, cobalt or nickel salts. The new compounds were characterized by elemental analysis, IR, ^{1}H, and ^{19}F NMR and UV–Vis spectroscopy as well as mass spectrometry. The fluoroether substituted Pcs are best soluble in polar solvents such as acetone and THF.

1. Introduction

Phthalocyanines and their metal complexes have found application in different areas of research, such as photoreceptors in photographic printing [1], thin film organic transistors [2], photovoltaic cells [3], liquid crystals [4–6], photodynamic therapy [7–12], light-emitting diodes [13] and chemical sensors [14–20]. Phthalocyanines are among the most widely used chemically sensitive coating materials in chemical sensors [21] and suitable for detecting volatile organic compounds (VOCs) in gas and liquid phase [22].

The physico-chemical properties of phthalocyanines can be modified in a wide range through chemical modifications made to the Pc core structure. For example, the solubility in organic solvents is increased by the introduction of bulky or long chain alkyl or alkoxy groups to the periphery of the macrocycle. Tetra substituted Pcs are commonly found to exhibit a higher solubility than the octa substituted ones [23–25]. The formation of constitutional isomers during synthesis of the tetra substituted phthalocyanines leads to the higher solubility of these systems [26].

In the past decade, a new generation of phthalocyanines with fluorinated, electron withdrawing substituents has been developed [27–29]. These Pcs are of much interest due to their high solubility in polar solvents such as acetone or THF. The electronic properties are widely affected by introducing electron donor or acceptor groups, as well. While unsubstituted phthalocyanines exhibit p-type behavior MePcF16 shows n-type behavior due to the electron withdrawing properties of the strongly electronegative fluorine atoms directly attached to the Pc core [30–34]. Phthalocyanines with electron donating or electron withdrawing substituents were studied in photovoltaic cells or gas sensors [35–38]. Furthermore, the properties of phthalocyanines are influenced not only by the nature of the substituents (electron donating or electron withdrawing) on the phthalocyanine and substitution pattern (tetra, octa, peripheral, non-peripheral), but also by the nature of the metal ion complex.

In this paper, we present for the first time the synthesis and characterization of phthalocyanines substituted with fluoroethers as electron withdrawing substituents. Aggregation properties of the phthalocyanine derivatives in different solvents and at different concentrations in chloroform are also presented.

2. Result and discussion

The compound **1** was prepared by nucleophilic substitution of the nitro group in 4-nitrophthalonitrile with 1H,1H-nonafluoro-3,6-dioxaheptan-1-ol. The compounds **2** and **3** were both prepared by the reaction of 1H,1H-nonafluoro-3,6-dioxaheptan-1-ol with 4,5-dichlorophthalonitrile (Fig. 1). They were separated from the same reaction mixture, but the yield ratio of the two products was found to change with reaction temperature. In case of a reaction temperature of near 95 °C compound **3** was obtained in higher yields than **2**.

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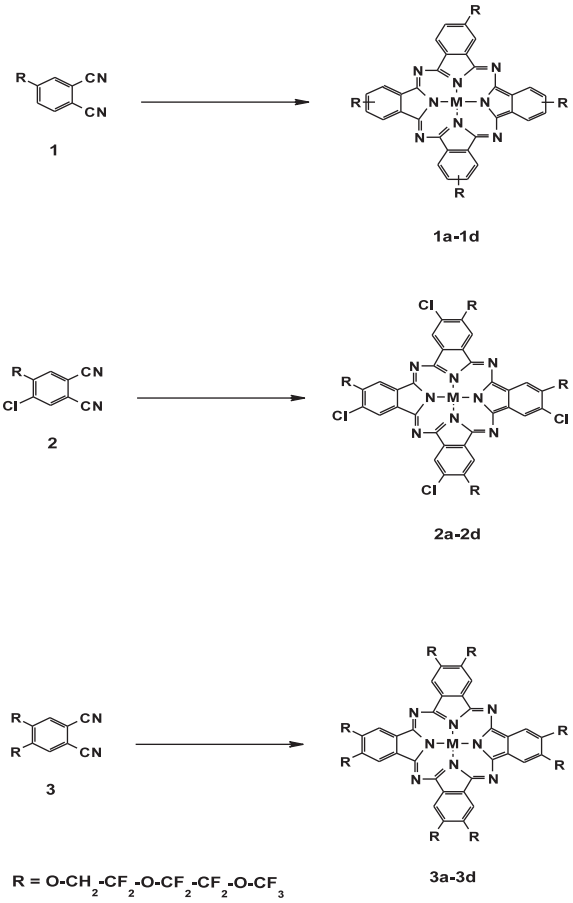
0022-1139/$ – see front matter.
http://dx.doi.org/10.1016/j.jfluchem.2012.06.023



Compound	M
1a, 2a, 3a	Zn(II)
1b, 2b, 3b	Co(II)
1c, 2c, 3c	2H
1d, 2d, 3d	Ni(II)

Fig. 1. Synthesis routes of substituted phthalocyanine derivatives.

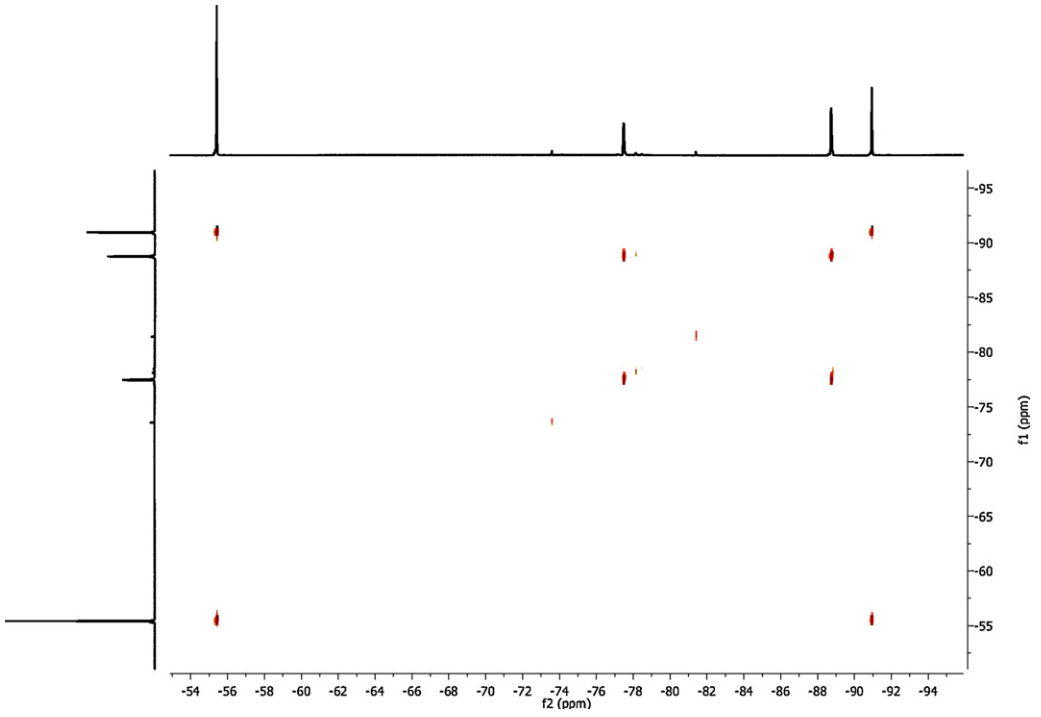


Fig. 2. ^{19}F COSY spectrum of compound **3**.

All the phthalocyanines were obtained by the cyclotetramerization of a phthalonitrile and synthesized according to reported methods [39–46]. The synthesis of both the octa and tetra substituted metal phthalocyanines (**1a**–**3a**, **1b**–**3b**, **1d**–**3d**) was achieved in anhydrous amyl alcohol using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base in the presence of anhydrous zinc(II) acetate, cobalt(II) chloride or nickel(II) chloride, respectively, at 140 °C under an argon atmosphere (Fig. 1). The metal free phthalocyanines **1c**, **2c** and **3c** were obtained directly by refluxing **1**, **2** or **3** in 2-(dimethyl-amino)ethanol. The new intermediate products and phthalocyanines were characterized by ^{1}H NMR, ^{19}F NMR, FT-IR, and UV–vis spectrometry, elemental analysis, and MS. The spectroscopic data for the newly synthesized compounds were consistent with the assigned formulation. The results are given in the Section 4.

Purification of all the studied phthalocyanines was done by column chromatography over silica gel using THF or acetone as eluents.

We have observed that the solubility of the perfluoroethoxy phthalocyanines is affected by both the central metal ion and the number of substituents. While **1a** and **1b** are soluble in non-polar organic solvents (e.g. chloroform), **2a**, **3a**, **2b** and **3b** show high solubility only in polar organic solvents such as THF, acetone, and DMSO. **1c**–**3c** and **1d**–**3d** are not soluble in chloroform, THF, acetone, and DMSO. Generally, fluoroalkyl substituted compounds are known to have high solubility in polar solvents [47].

The IR spectra of the compounds **1**, **2,** and **3** clearly indicate the presence of C≡N groups by the intense stretching bands around 2235 cm^{-1}. The characteristic C–F bands of **1**, **2** and **3** appeared at 1180 cm^{-1}.

Generally, while the phthalocyanines are prepared by cyclotetramerization of substituted phthalonitriles, generally the imide occurred and observed as the characteristic band at around 1700 cm^{-1} in IR absorptions. The absence of this band is attributed to the purity of the phthalocyanine which supports the information observed from the thin layer chromatography (TLC). The absence of the inner –NH band (3300 cm^{-1}) (characteristic for H_2Pc) confirms the metallic Pc structure.

In the ^{1}H NMR spectrum of **1** the aromatic protons appeared at δ 8.08 (d), 7.85 (d) and 7.66 (dd). The CH_2 protons of the substituent group were observed at 5.06 ppm as a triplet due to the effect of the fluorine atoms. The spectra of **2** and **3** were observed as expected in accordance with the proposed structure. The tetrasubstituted phthalocyanines were obtained as a mixture of the four possible structural isomers. For this reason, the ^{1}H NMR spectra of **1a** and **2a** have broad bands [48,49].

The coupling between hydrogen–fluorine and fluorine–fluorine atoms make the interpretation of the ^{19}F NMR spectra difficult. For this reason, the ^{19}F NMR peaks of compound **3** are assigned based on a ^{19}F COSY experiment (Fig. 2). The signals along the diagonal reflect the normal ^{19}F spectrum. The cross peaks provide the necessary information for peak assignment. In general, each cross peak represents a correlation due to either three or four bond F–F coupling. The observed cross peaks indicate the following correlations: CF_3 with O–CF_2 and CF_2–O with O–CF_2CH_2. In the ^{19}F COSY spectrum of compound **3** no $^{3}J_{FF}$ correlation was observed [50].

The spectra of the compounds **1**, **2** and **3** showed the characteristic peaks of the nine fluorine atoms of the substituent groups. The peaks assigned to the CF_3, CF_2CH_2, CF_3–O–CF_2–**CF_2**–O, CF_3–O–**CF_2** fragment were observed at δ −56.21, −78.08, −89.21, and −91.59 ppm (Fig. 3), respectively. The CF_3 signals appeared as a triplet due to $^{4}J_{FF}$ coupling of the fluorine atoms ($^{4}J_{FF}$ = 9 Hz). The **CF_2**–CH_2 signals are split as a multiplet due to $^{4}J_{FF}$ and $^{3}J_{HF}$ coupling (9 Hz and 13 Hz, respectively). Area integration of the four observed peaks yielded the expected 3:2:2:2 ratio. ^{19}F NMR spectra of the phthalocyanines feature the same characteristic chemical shifts as for compound **3**.

In addition to these positive results supporting the expected chemical structures the mass spectra of compounds **1**, **2** and **3** gave the characteristic molecular ion peaks at *m*/*z* 408 [M]$^{+}$, 442 [M]$^{+}$, 688 [M]$^{+}$ respectively, as a second confirmation. Concerning the phthalocyanines intense singly charged molecular ions peaks were

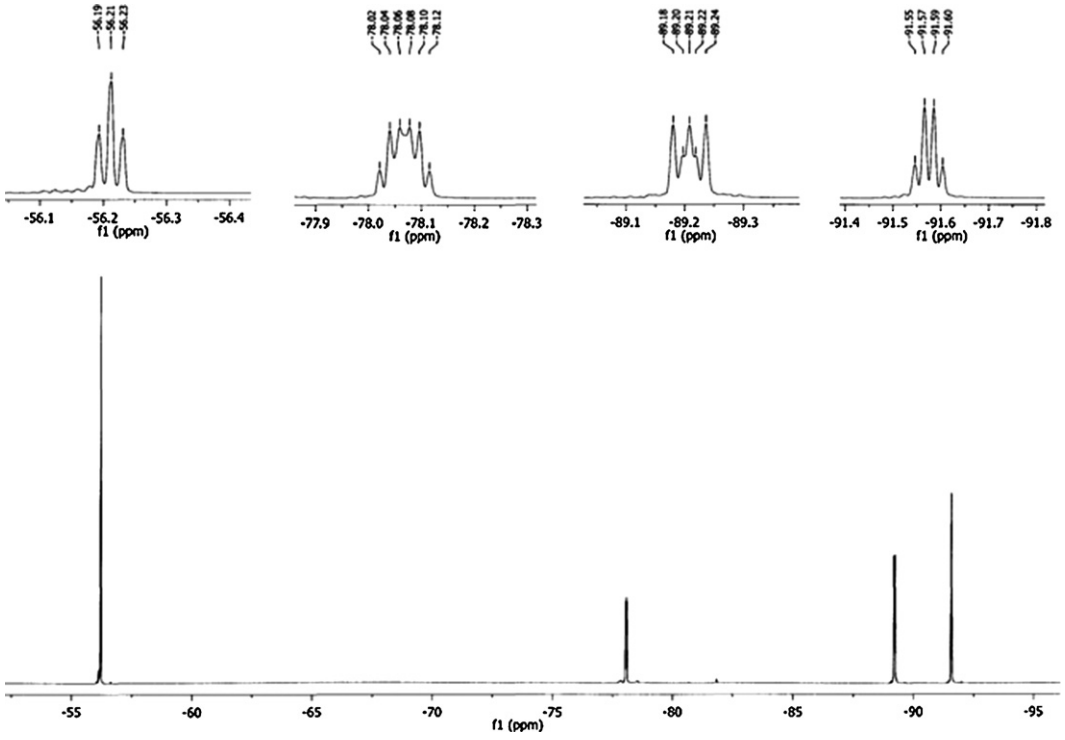


Fig. 3. ^{19}F NMR spectrum of compound **3**.

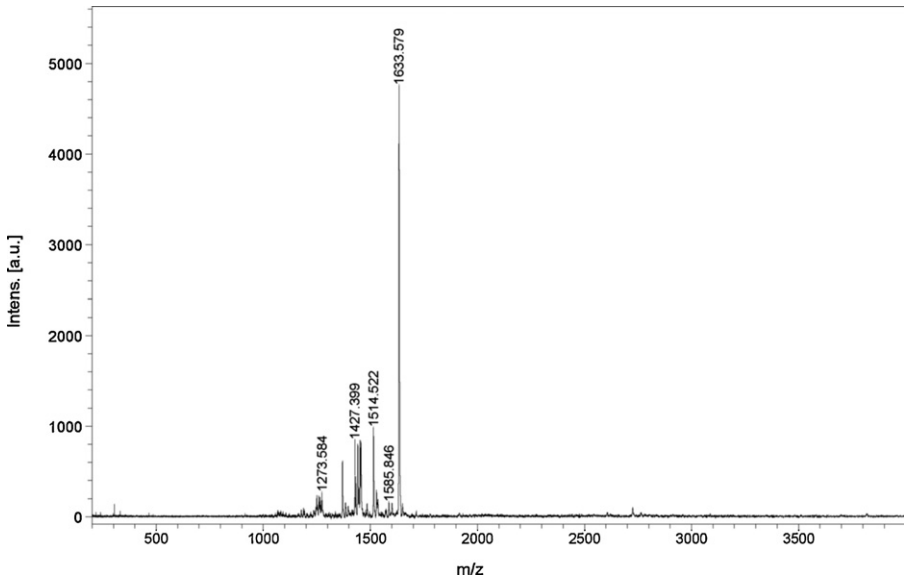


Fig. 4. Positive ion MALDI-MS spectrum of **1c** obtained in DHB matrix.

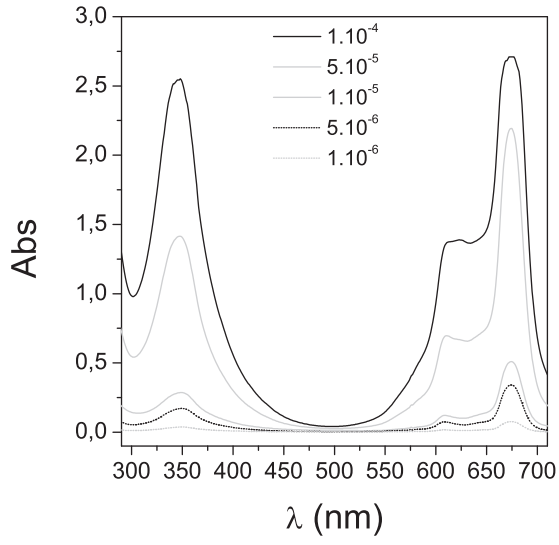


Fig. 5. UV–vis spectra of **1a** in $CHCl_3$ at different concentrations: 1×10^{-4}, 5×10^{-5}, 1×10^{-5}, 5×10^{-6}, 1×10^{-6} M.

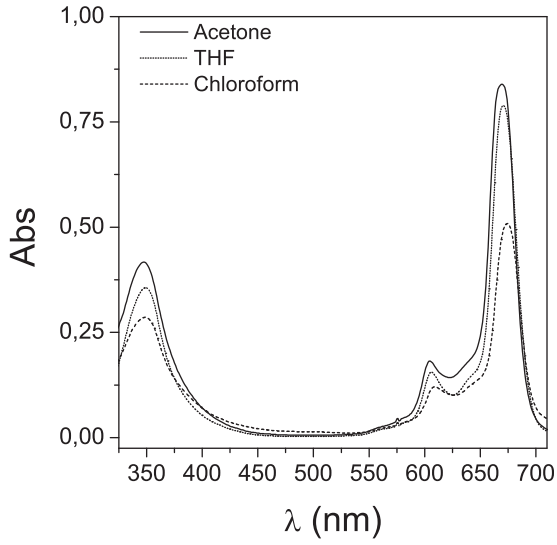


Fig. 6. UV–vis spectra of **1a** in different solvents: acetone (-), THF (–), chloroform (. . .).

observed in all cases in the MALDI-TOF spectra with 2,5-dihydroxy benzoic acid (DHB) as matrix. The positive ion MALDI-MS spectrum of **1c** is given in Fig. 4.

In order to investigate the photophysical properties of the synthesized compounds, UV–vis absorption spectra were recorded. The phthalocyanines exhibit typical spectra with two strong absorption regions. One of them is the so-called Soret Band (B Band) in the UV region at around 300–350 nm and the other is the *Q* band in the visible region at 600–700 nm. The UV–vis spectra of the phthalocyanine complexes **1a**, **1b**, **2a**, **2b**, **3a**, **3b** exhibited characteristic absorptions in the *Q*-band region at around 671, 659, 670, 658, 667, 655 nm in THF, respectively. The absorption maximum is blue-shifted about 12 nm (e.g. from 671 nm for **1a** to 659 nm for **1b** in THF) and absorption coefficient becomes lower (from 4.90 for **1a** to 4.65 for **1b**) as the result of the change in the central metal ion. Their *Q* band wavelengths were attributed to the π–π^* transition from the HOMO to the LUMO of the Pc^{2-} ring. The *Q* band of the octa substituted Pc (**3b**) (655 nm) is shifted to lower wavelengths compared with that of the tetra substituted Pc (**1b**) (659 nm) due to the difference of substitution pattern. The *Q* band positions of the perfluoroethoxy substituted MPcs result from the electron withdrawing effect of the fluorine atoms in the substituents. The *Q* bands of other compounds were comparable to those of the compounds **1b** and **3b**.

Furthermore, the aggregation behavior of **1a** was investigated at different concentrations in chloroform (Fig. 5). The intensity of the *Q* band absorption increased in parallel with increasing concentration. The Lambert–Beer law was obeyed for compound **1a** for concentrations ranging from 1×10^{-4} to 1×10^{-6} M.

In addition, the visible absorption spectra illustrating the aggregation behavior of phthalocyanines in various solvents are shown in Fig. 6. In THF an intense absorption band at 670 nm and a shoulder around 605 nm are observed. The low-energy band has been attributed to unaggregated phthalocyanine and the high-energy shoulder to aggregated species [1,36]. On the contrary to the results in THF and acetone, in apolar solvents such as chloroform the high energy band around 674 nm was not observed in the spectra, which has been assigned to the non aggregated

phthalocyanine species as encountered in a number of soluble phthalocyanines [51,52].

3. Conclusion

In this paper, we have prepared and characterized Zn(II), Ni(II), Co(II) and 2H phthalocyanine complexes substituted with 1H,1H-nonafluoro-3,6-dioxaheptan-1-ol in tetra and octa positions for the first time. The presented spectroscopic and analytical results confirm that all compounds have their proposed structures. Fluorine atoms in the structure increase the solubility of the complexes in acetone and THF. We also studied the aggregation behavior of the new complexes **1a**, **1b**, **2a**, **2b**, **3a**, and **3b** in different solvents and also of **1a** at different concentrations in chloroform. The substituted complexes showed similar typical aggregation behavior. However, tetra and octa fluoroxy substitution of phthalocyanines have proved to be an extremely efficient way to diminish aggregation among the planar molecules. The *Q*-band positions of the fluoroxy substituted MPcs result from the balance of some factors, such as the electron-withdrawing effect of the fluorine atoms in the substituents and the number (4 or 8) of the substituents on the Pc ring.

The sensor properties of these new compounds will be the subject of our future study.

4. Experimental

4.1. Characterization methods and chemicals

Elemental analyses were obtained using a Thermo Finnigan Flash 1112 instrument. Infrared spectra were recorded on a Perkin Elmer FT-IR System Spectrum BX. ^{1}H and ^{19}F NMR spectra were recorded in THF-d_8 solution on Bruker and Varian 500 MHz spectrometers. Absorption spectra in the UV–visible region were recorded with a Shimadzu 2001 UV spectrophotometer. The mass spectra were acquired with a Bruker Daltonics MicrOTOF mass spectrometer equipped with an electro spray ionization (ESI) source. The instrument was operated in positive ion mode using a *m/z* range of 50–3000. The capillary voltage of the ion source was set at 6000 V and the capillary exit at 190 V. The nebulizer gas flow 1 bar and drying gas flow 8 mL min^{-1}. Positive ion and linear mode MALDI-TOF MS spectra of the compounds were obtained in 2,5-dihydroxy benzoic acid as matrix using nitrogen laser accumulating 50 laser shots.

n-amyl alcohol and dimethylformamide (DMF) were dried according to literature procedures [53]. $NiCl_2$, $Zn(CH_3COO)_2$, $CoCl_2$, K_2CO_3, Na_2CO_3, anhydrous Na_2SO_4, THF-d_8, acetone-d_6 and 1H,1H-nonafluoro-3,6-dioxaheptan-1-ol were purchased from commercial suppliers. 4-nitrophthalonitrile [54], 4,5-dichlorophthalonitrile [55] were synthesized and purified according to the literature procedures.

4.2. Synthesis

4.2.1. 4-{2,2-Difluoro-2-[1,1,2,2-tetrafluoro-2-(trifluoromethoxy)ethoxy]ethoxy} phthalonitrile (**1**)

1H,1H-nonafluoro-3,6-dioxaheptan-1-ol (2.0 g, 7.1 mmol) was dissolved in absolute DMF (5 mL) under argon and 4-nitrophthalonitrile (1.2 g, 7.1 mmol) was added. After stirring for 10 min, finely ground anhydrous potassium carbonate (1.77 g, 13.0 mmol) was added in portions during 2 h with efficient stirring. The reaction mixture was stirred under argon atmosphere at 60 °C for 72 h. The solvent was evaporated under reduced pressure. Water (5 mL) was added and the aqueous phase was extracted with dichloromethane (3 mL × 10 mL). The combined extracts were treated first with sodium carbonate solution (5%), then with water and dried over anhydrous sodium sulfate. Dichloromethane was removed under reduced pressure. The pure product was obtained by crystallization from $CHCl_3$. The product was soluble in CH_2Cl_2, $CHCl_3$, acetone, MeOH, and DMSO.

Yield: 1.9 g (66%), m.p. 55–57 °C. FT-IR (cm^{-1}): 3096, 2235 (C≡N), 1603, 1568, 1495, 1458, 1435, 1276, 1254, 1179 (CF), 1140, 1078 (CO), 964. ^{1}H NMR (Acetone d_6): δ, ppm 8.08 (1H, d, ArH), 7.85 (1H, d, ArH), 7.66 (1H, dd, ArH), 5.06 (2H, t, CH_2). ^{19}F NMR (acetone d_6): δ, ppm −56.10 (t, CF_3, $^4J_{FF}$ = 9 Hz, $^5J_{FF}$ = 1.8 Hz), −78.82 (m, CF_2–CH_2, $^4J_{FF}$ = 9 Hz, $^3J_{HF}$ = 13 Hz), −89.12 (m, CF_2–O, $^4J_{FF}$ = 9 Hz), −91.52 (q, 2F, O–CF_2, $^4J_{FF}$ = 9 Hz). Calc. for $C_{13}H_5F_9N_2O_3$ (408.17): C 38.25; H 1.23; N 6.86; Found: C 37.53; H 1.18; N 6.69. MS (EI): *m/z* (%): 408 [M]$^+$.

4.2.2. 4-Chloro-5-{2,2-difluoro-2-[1,1,2,2-tetrafluoro-2-(trifluoromethoxy)ethoxy] ethoxy}phthalonitrile (**2**)

1H,1H-nonafluoro-3,6-dioxaheptan-1-ol (1.0 g, 3.6 mmol) was dissolved in absolute DMF (5 mL) under argon and 4,5-dichlorophthalonitrile (0.71 g, 3.6 mmol) was added. After stirring for 10 min finely ground anhydrous potassium carbonate (2.94 g, 21.0 mmol) was added in portions during 2 h with efficient stirring. The reaction mixture was stirred under argon atmosphere at 70 °C for 72 h. The solvent was evaporated under reduced pressure. Water (5 mL) was added and the aqueous phase was extracted with dichloromethane (3 × 10 cm^3). The combined extracts were treated first with sodium carbonate solution (5%), then with water and dried over anhydrous sodium sulfate. Dichloromethane was removed under reduced procedure. The product was purified by column chromatography on silica gel using *n*-hexan/dichloromethane (1:1) as the eluent. The product is soluble in CH_2Cl_2, $CHCl_3$, acetone, MeOH and DMSO.

Yield: 0.83 g (52%), m.p. 41–43 °C. FT-IR (cm^{-1}): 3048, 2235(CN), 1584, 1498, 1448, 1392, 1272, 1182 (CF), 1064 (CO), 969. ^{1}H NMR (acetone d_6): δ, ppm 8.06 (1H, s, ArH), 7.84 (1H, s, ArH), 4.94 (1H, t, ArH). ^{19}F NMR (acetone d_6): δ, ppm −56.11 (t, CF_3, $^4J_{FF}$ = 9 Hz, $^5J_{FF}$ = 1.5 Hz), −77.85 (m, **CF_2**–CH_2, $^4J_{FF}$ = 9 Hz, $^3J_{HF}$ = 13 Hz) −89.17 (m, CF_2–O, $^4J_{FF}$ = 13 Hz), −91.54 (q, 2F, O–CF_2, $^4J_{FF}$ = 9 Hz). Calc. for $C_{13}H_4ClF_9N_2O_3$ (442.62): C 35.28; H 0.91; N 6.33; Found: C 35.12; H 0.87; N 6.14. MS (EI): *m/z* (%): 442 [M]$^+$.

4.2.3. 4,5-Bis{2,2-difluoro-2-[1,1,2,2-tetrafluoro-2-(trifluoromethoxy)ethoxy]ethoxy} phthalonitrile (**3**)

1H,1H-nonafluoro-3,6-dioxaheptan-1-ol (4.0 g, 14.2 mmol) was dissolved in absolute DMF (5 mL) under argon and 4,5-dichlorophthalonitrile (1.3 g, 7.1 mmol) was added. After stirring for 10 min, finely ground anhydrous potassium carbonate (3.70 g, 27.0 mmol) was added in portions during 2 h with efficient stirring. The reaction mixture was stirred under argon atmosphere at 95 °C for 72 h. The solvent was evaporated under reduced pressure. Water (5 mL) was added and the aqueous phase was extracted with dichloromethane (3 mL × 10 mL). The combined extracts were treated first with sodium carbonate solution (5%), then with water and dried over anhydrous sodium sulfate. Dichloromethane was removed under reduced pressure. The product was purified by column chromatography on silica gel using *n*-hexan/dichloromethane (1:1) as the eluent. The product was soluble in CH_2Cl_2, $CHCl_3$, acetone, MeOH, and DMSO.

Yield: 1.30 g (27%), m.p. 69–70 °C. FT-IR (cm^{-1}): 3048, 2235(CN), 1588, 1499, 1452, 1390, 1272, 1215, 1182 (CF), 1137, 1096 (CO), 972. ^{1}H NMR (acetone d_6): δ, ppm 7.90 (2H, s, ArH), 5.04 (4H, t, CH_2). ^{19}F NMR (acetone d_6): δ, ppm −56.21 (t, CF_3, $^4J_{FF}$ = 9 Hz), −78.08 (m, **CF_2**–CH_2, $^4J_{FF}$ = 9 Hz, $^3J_{HF}$ = 13 Hz), −89.21 (m, CF_2–O, $^4J_{FF}$ = 13 Hz), −91.59 (q, 2F, O–CF_2, $^4J_{FF}$ = 9 Hz). Calc. for $C_{18}H_6F_{18}N_2O_6$ (688.23): C 31.41; H 0.88; N 4.07; Found: C 31.33; H 0.89; N 4.01. MS (MS-EI): *m/z* (%): 688 [M]$^+$.

*4.2.4. Compound **1a***

Compound **1** (0.5 g, 1.22 mmol) and anhydrous $Zn(CH_3COO)_2$ (0.056 g, 0.31 mmol), and 0.2 mL DBU in 5 mL *n*-amyl alcohol were heated to 140 °C for 7 h under an argon atmosphere in a round-bottomed flask. The resulting green crude product was cooled and filtered. The crude product was purified by passing through a silica gel column using acetone and THF as eluents.

Yield: 250 mg (48%), m.p. > 200 °C. FT-IR (cm^{-1}): 2960, 1609, 1488, 1396, 1339, 1221, 1178(CF), 1100(CO), 968. ^{1}H NMR (THF d_8): δ, ppm 8.79 (4H, b, ArH), 8.44 (4H, b, ArH), 7.65 (4H, b, ArH), 5.08 (8H, t, CH_2). ^{19}F NMR (THF d_8): δ, ppm −54.33 (p, 12F, CF_3, $^4J_{FF}$ = 9 Hz), −75.80 (m, 8F, **CF_2**–CH_2, $^4J_{FF}$ = 9 Hz, $^3J_{HF}$ = 13 Hz), −87.05 (m, 8F, CF_2–O, $^4J_{FF}$ = 9 Hz), −89.50 (m, 8F, O–CF_2, $^4J_{FF}$ = 9 Hz). Calc. for $C_{52}H_{20}F_{36}N_8O_{12}Zn$ (1698.09): C 36.78; H 1.19; N 6.60; Found: C 36.75; H 1.13; N 6.60. UV–vis (THF): λ_{max}/nm (log ε): 349 (4.55), 671 (4.90). MS (MS-MALDI): *m/z* (%): 1698 $[M]^+$.

*4.2.5. Compound **1b***

Compound **1b** was prepared according to the procedure described for **1a**. The amounts of reagents employed were as follows: **1** (0.5 g, 1.22 mmol) and anhydrous cobalt(II) chloride (0.04 g, 0.31 mmol) in 3 mL ethylene glycol.

Yield: 130 mg (25%), m.p. 194 °C. FT-IR (cm^{-1}): 2949, 1612, 1480, 1410, 1222, 1178 (CF), 1100 (CO), 968. ^{19}F NMR (THF d_8): δ, ppm −54.44 (p, 12F, CF_3, $^4J_{FF}$ = 9 Hz), −75.93 (m, 8F, **CF_2**–CH_2, $^4J_{FF}$ = 9 Hz, $^3J_{HF}$ = 13 Hz), −87.30 (m, 8F, CF_2–O, $^4J_{FF}$ = 9 Hz), −89.73 (m, 8F, O–CF_2, $^4J_{FF}$ = 9 Hz). Calc. for $C_{52}H_{20}F_{36}N_8O_{12}Co$ (1691.94): C 36.92; H 1.19; N 6.62; Found: C 36.86; H 1.18; N 6.60. UV–vis (THF): λ_{max}/nm (log ε): 330 (4.49), 659 (4.65). MS (MS-MALDI): *m/z* (%): 1691 $[M]^+$.

*4.2.6. Compound **1c***

Compound **1c** was prepared according to the procedure described for 1**a**. The amounts of reagents employed and conditions were as follows: **1** (0.5 g, 1.22 mmol) in 1 mL dry 2-(dimethyl-amino)ethanol at 175 °C.

Yield: 160 mg (32%), m.p. > 200 °C. FT-IR (cm^{-1}): 3046, 2963, 1615, 1483, 1222, 1180 (CF), 1100 (CO), 969. Calc. for $C_{52}H_{22}F_{36}N_8O_{12}$ (1634.72): C 38.21; H 1.36; N 6.85; Found: C 37.52; H 1.28; N 6.22. MS (MS-MALDI): *m/z* (%): 1634 $[M]^+$.

*4.2.7. Compound **1d***

Compound **1d** was prepared according to the procedure described for **1a**. The amounts of reagents employed were as follows: **1** (0.3 g, 0.73 mmol), anhydrous nickel(II) chloride (0.024 g, 0.18 mmol), and 0.2 mL DBU in 4 mL *n*-amyl alcohol.

Yield: 95 mg (31%), m.p. > 200 °C. FT-IR (cm^{-1}): 2935, 1611, 1470, 1224, 1175 (CF), 1109 (CO), 967. Calc. for $C_{52}H_{20}F_{36}N_8O_{12}Ni$ (1691.40): C 36.92; H 1.19; N 6.62; Found: C 36.73; H 1.16; N 6.58. MS (MS-MALDI): *m/z* (%): 1691 $[M]^+$.

*4.2.8. Compound **2a***

Compound **2a** was prepared according to the procedure described for 1**a**. The amounts of reagents employed were as follows: **2** (0.5 g, 1.13 mmol), anhydrous zinc(II) acetate (0.055 g, 0.27 mmol), and 0.2 mL DBU in 5 mL *n*-amylalcohol.

Yield: 210 mg (42%), m.p. > 200 °C. FT-IR (cm^{-1}): 2952, 1607, 1487, 1440, 1391, 1220, 1178 (CF), 1138, 1068 (CO), 968. ^{1}H NMR (THF d_8): δ, ppm 8.96 (4H, s, ArH), 8.54 (4H, s, ArH), 5.40 (8H, s, CH_2). ^{19}F NMR (THF d_8): δ, ppm −54.40 (m, 12F, CF_3, $^4J_{FF}$ = 9 Hz), −76.16 (m, 8F, **CF_2**–CH_2, $^4J_{FF}$ = 9 Hz, $^3J_{HF}$ = 13 Hz), −87.35 (m, 8F, CF_2–O, $^4J_{FF}$ = 9 Hz), −89.51 (m, 8F, O–CF_2, $^4J_{FF}$ = 9 Hz). Calc. for $C_{52}H_{16}Cl_4F_{36}N_8O_{12}Zn$ (1835.91): C 34.02; H 0.88; N 6.10; Found: C 34.05; H 0.86; N 6.03. UV–vis (THF): λ_{max}/nm (log ε): 354 (4.67), 670 (5.04). MS (MS-MALDI): *m/z* (%): 1835 $[M]^+$.

*4.2.9. Compound **2b***

Compound **2b** was prepared according to the procedure described for **2a**. The amounts of reagents employed were as follows: **2** (0.3 g, 0.68 mmol) and anhydrous cobalt(II) chloride (0.022 g, 0.17 mmol) in 2 mL ethylene glycol.

Yield: 120 mg (38%), m.p. > 200 °C. FT-IR (cm^{-1}): 2933, 1608, 1526, 1446, 1405, 1218, 1177(CF), 1137, 1072 (CO), 962. ^{19}F NMR (THF d_8): δ, ppm −54.25 (t, 12F, CF_3, $^4J_{FF}$ = 9 Hz), −75.21 (m, 8F, **CF_2**–CH_2, $^4J_{FF}$ = 9 Hz, $^3J_{HF}$ = 13 Hz), −86.77 (m, 8F, CF_2–O, $^4J_{FF}$ = 9 Hz), −89.23 (m, 8F, O–CF_2, $^4J_{FF}$ = 9 Hz). Calc. for $C_{52}H_{16}Cl_4F_{36}N_8O_{12}Co$ (1829.45): C 34.14; H 0.88; N 6.13; Found: C 34.13; H 0.80; N 6.09. UV–vis (THF): λ_{max}/nm (log ε): 336 (4.63), 658 (4.75). MS (MS-MALDI): *m/z* (%): 1829 $[M]^+$.

*4.2.10. Compound **2c***

Compound **2c** was prepared according to the procedure described for **2a**. The amounts of reagents employed were as follows: **2** (0.25 g, 0.56 mmol) in 1 mL 2-(dimethyl-amino)ethanol.

Yield: 14 mg (6%), m.p. > 200 °C. FT-IR (cm^{-1}): 3048, 2936, 1610, 1447, 1392, 1221, 1180 (CF), 1100 (CO), 1020, 970. Calc. for $C_{52}H_{18}Cl_4F_{36}N_8O_{12}$ (1772.51): C 35.24; H 1.02; N 6.32; Found: C 29.28; H 1.50; N 5.11. MS (MS-MALDI): *m/z* (%): 1772 $[M]^+$.

*4.2.11. Compound **2d***

Compound **2d** was prepared according to the procedure described for **2a**. The amounts of reagents employed were as follows: **2** (0.4 g, 0.9 mmol), anhydrous nickel(II) chloride (0.029 g, 0.22 mmol) and 0.2 mL DBU in 4 mL *n*-amyl alcohol.

Yield: 60 mg (15%), m.p. > 200 °C. FT-IR (cm^{-1}): 3047, 2947, 1608, 1447, 1392, 1221, 1180(CF), 1100 (CO), 1020, 970. Calc. for $C_{52}H_{16}Cl_4F_{36}N_8O_{12}Ni$ (1829.18): C 34.14; H 0.88; N 6.13; Found: C 34.12; H 0.84; N 5.98. MS (MS-MALDI): *m/z* (%): 1829 $[M]^+$.

*4.2.12. Compound **3a***

Compound **3a** was prepared according to the procedure described for **2a**. The amounts of reagents employed were as follows: **3** (0.4 g, 0.58 mmol), anhydrous zinc(II) acetate (0.027 g, 0.15 mmol) and 0.2 mL DBU in 5 mL *n*-amylalcohol.

Yield: 130 mg (31%), m.p. > 200 °C. FT-IR (cm^{-1}): 2963, 1612, 1493, 1454, 1341, 1224, 1178 (CF), 1070 (CO), 962. ^{1}H NMR (THF d_8): δ, ppm 9.12 (8H, s, ArH), 5.44 (16H, s, CH_2). ^{19}F NMR (THF d_8): δ, ppm −54.56 (m, 24F, CF_3, $^4J_{FF}$ = 9 Hz), −76.91 (m, 16F, **CF_2**–CH_2), −87.30 (m, 16F, CF_2–O), −89.73 (m, 16F, O–CF_2). Calc. for $C_{72}H_{24}F_{72}N_8O_{24}Zn$ (2818.33): C 30.68; H 0.86; N 3.98; Found: C 30.62; H 0.85; N 3.97. UV–vis (THF): λ_{max}/nm (log ε): 355 (4.24), 667 (5.05). MS (MS-MALDI): *m/z* (%): 2818 $[M]^+$.

*4.2.13. Compound **3b***

Compound **3b** was prepared according to the procedure described for **3a**. The amounts of reagents employed were as follows: **3** (0.4 g, 0.58 mmol) and anhydrous cobalt(II) chloride (0.019 g, 0.15 mmol) in 3 mL ethylene glycol.

Yield: 55 mg (14%), m.p. > 200 °C. FT-IR (cm^{-1}): 2932, 1609, 1472, 1430, 1224, 1180 (CF), 1100 (CO), 962. ^{19}F NMR (THF d_8): δ, ppm −56.32 (m, 24F, CF_3, $^4J_{FF}$ = 9 Hz), −78.48 (m, 16F, **CF_2**–CH_2), −89.07 (m, 16F, CF_2–O), −91.35 (m, 16F, O–CF_2). Calc. for $C_{72}H_{24}F_{72}N_8O_{24}Co$ (2811.88): C 30.75; H 0.86; N 3.99; Found: C 30.39; H 0.80; N 3.95. UV–vis (THF): λ_{max}/nm (log ε): 335 (4.62), 655 (4.76). MS (MS-MALDI): *m/z* (%): 2811 $[M]^+$.

*4.2.14. Compound **3c***

Compound **3c** was prepared according to the procedure described for **3a**. The amounts of reagents employed were as follows: **3** (0.25 g, 0.36 mmol) in 1 mL 2-(dimethyl-amino)ethanol.

Yield: 30 mg (12%), m.p. > 200 °C. FT-IR (cm^{-1}): 3048, 2956, 1612, 1499, 1451, 1225, 1180 (CF), 1136, 1096 (CO), 972. Calc. for

$C_{72}H_{26}F_{72}N_8O_{24}$ (2754.90): C 31.39; H 0.95; N 4.07; Found: C 31.28; H 0.97; N 3.98. MS (MS-MALDI): *m/z* (%): 2754 $[M]^+$.

4.2.15. Compound **3d**

Compound **3d** was prepared according to the procedure described for **3a**. The amounts of reagents employed were as follows: **3** (0.4 g, 0.58 mmol), anhydrous nickel(II) chloride (0.019 g, 0.15 mmol), and 0.2 mL DBU in 4 mL *n*-amyl alcohol.

Yield: 95 mg (23%), m.p. $> 200\,^{\circ}C$. FT-IR (cm^{-1}): 2956, 1612, 1478, 1452, 1272, 1224, 1180 (CF), 1093 (CO), 962. Calc. for $C_{72}H_{24}F_{72}N_8O_{24}Ni$ (2811.58): C 30.76; H 0.86; N 3.99; Found: C 30.72; H 0.83; N 3.97. MS (MS-MALDI): *m/z* (%): 2811 $[M]^+$.

References

[1] (a) C.C. Leznoff, A.B.P. Lever, Phthalocyanines: Properties and Applications, VCH, New York, NY, 1989–1996;
(b) N.B. McKeown, Phthalocyanine Materials: Synthesis, Structure and Function, Cambridge University Press, Cambridge, 1998.
[2] W. Wu, H. Zhang, Y. Wang, S. Ye, Y. Guo, C. Di, G. Yu, D. Zhu, Y. Liu, Advanced Functional Materials 18 (2008) 2593–2601.
[3] S. Eu, T. Katoh, T. Umeyama, Y. Matano, H. Imahori, Dalton Transactions 40 (2008) 5476–5483.
[4] C.F. Van Nostrum, S.J. Picken, A.J. Schouten, R.J.M. Nolte, Journal of the American Chemical Society 117 (1995) 9957–9965.
[5] Z.Z. Öztürk, N. Kiliç, D. Atilla, A.G. Gürek, V. Ahsen, Journal of Porphyrins and Phthalocyanines 13 (2009) 1179–1187.
[6] H. Lino, J. Hanna, R.J. Bushby, B. Movaghar, B.J. Whitaker, M.J. Cook, Applied Physics Letters 87 (2005), 132102-1–132102-3.
[7] M.J. Cook, I. Chambrier, Journal of Porphyrins and Phthalocyanines 15 (2011) 149–173.
[8] L.M. Moreira, F.V. dos Santos, J.P. Lyon, M. Maftoum-Costa, C. Pacheco-Soares, N.S. Silva, Australian Journal of Chemistry 61 (2008) 741–754.
[9] S.A. Gorman, S.B. Brown, J. Griffiths, Journal of Environmental Pathology Toxicology and Oncology 25 (2006) 79–108.
[10] R. Bonnett, Chemical Society Reviews 24 (1995) 19–33.
[11] J.D. Spikes, Journal of Fluorine Chemistry 113 (2002) 161–165.
[12] L. Gao, X. Qian, Journal of Porphyrins and Phthalocyanines 13 (2009) 681–690.
[13] H.T. Lu, C.C. Tsou, M. Yokoyama, Electrochem, Solid State Letters 11 (2008) J31–J38.
[14] T. Sizun, M. Bouvet, Y. Chen, J.M. Suisse, G. Barochi, J. Rossignol, Sensors and Actuators B 159 (2011) 163–170.
[15] A.L. Sousa, W.J.R. Santos, R.C.S. Luz, F.S. Damos, L.T. Kubota, A.A. Tanaka, S.M.C.N. Tanaka, Talanta 75 (2008) 333–338.
[16] F.I. Bohrer, C.N. Colesniuc, J. Park, I.K. Schuller, A.C. Kummel, W.C. Trogler, Journal of the American Chemical Society 130 (2008) 3712–3713.
[17] T.V. Basova, C. Taşaltın, A.G. Gürek, M.A. Ebeoğlu, Z.Z. Öztürk, V. Ahsen, Sensors and Actuators B 96 (2003) 70–75.
[18] M. Harbeck, D. Erbahar, I. Gürol, E. Musluoğlu, V. Ahsen, Z.Z. Öztürk, Sensors and Actuators B 155 (2011) 298–303.
[19] M.L. Rodríguez-Méndez, Y. Gorbunova, J.A. Saja, Langmuir 18 (2002) 9560–9565.
[20] W. Göpel, Synthetic Metals 41 (1991) 1087–1093.
[21] J. Spadavecchia, G. Ciccarella, T. Stomeo, R. Rella, S. Capone, P. Siciliano, Chemistry of Materials 16 (2004) 2083–2090.
[22] (a) Z.Z. Öztürk, R. Zhou, V. Ahsen, Ö. Bekaroğlu, W. Göpel, Sensors and Actuators B 35 (1996) 404–408;
(b) M. Harbeck, D. Erbahar, I. Gürol, E. Musluoglu, V. Ahsen, Z.Z. Öztürk, Sensors and Actuators B 150 (2010) 346–354.
[23] M. Hanack, M. Lang, Advanced Materials 6 (1994) 819–833.
[24] P. Tau, T. Nyokong, Dalton Transactions 34 (2006) 4482–4490.
[25] A. Beck, K.M. Mangold, M. Hanack, Chemische Berichte 124 (1991) 2315–2321.
[26] D.K. Modibane, T. Nyokong, Polyhedron 28 (2009) 1475–1480.
[27] H. Yoshiyama, N. Shibata, T. Sato, S. Nakamura, T. Toru, Chemical Communications 7 (2008) 1977–1979.
[28] H. Yoshiyama, N. Shibata, T. Sato, S. Nakamura, T. Toru, Organic and Biomolecular Chemistry 7 (2009) 2265–2269.
[29] B. Das, M. Umeda, E. Tokunaga, T. Toru, N. Shibata, Chemistry Letters 39 (2010) 337–339.
[30] E. Kol'tsov, T. Basova, P. Semyannikov, I. Igumenov, Materials Chemistry and Physics 86 (2004) 222–227.
[31] D. Sukeguchi, H. Yoshiyama, N. Shibata, S. Nakamura, T. Toru, Y. Hayashi, T. Soga, Journal of Fluorine Chemistry 130 (2009) 361–364.
[32] N. Kobayashi, N. Sasaki, Y. Higashi, T. Osa, Inorganic Chemistry 34 (1995) 1636–1637.
[33] N. Kobayashi, H. Ogata, N. Nonaka, E.A. Luk'yanets, Chemistry – A European Journal 9 (2003) 5123–5134.
[34] M.R. Reddy, N. Shibata, Y. Kondo, S. Nakamura, T. Toru, Angewandte Chemie International Edition 45 (2006) 8163–8166.
[35] M. Bouvet, A. Pauly, Molecular semiconductor-based gas sensors, The Encyclopedia of Sensors (2006) 227–270.
[36] M. Bouvet, G. Guillaud, A. Leroy, A. Maillard, S. Spirkovitch, F.-G. Tournilhac, Sensors and Actuators B 73 (2001) 63–70.
[37] B. Das, E. Tokunaga, N. Shibgata, N. Kobayashi, Journal of Fluorine Chemistry 131 (2010) 652–654.
[38] N. Shibata, B. Das, E. Tokunaga, M. Shiro, N. Kobayashi, Chemistry – A European Journal 16 (2010) 7554–7562.
[39] T. Sugimori, S. Horike, M. Handa, K. Kasuga, Inorganica Chimica Acta 278 (1998) 253–255.
[40] J. Sleven, C. Görller, K. Binnemans, Materials Science and Engineering C 18 (2001) 229–238.
[41] D. Masurel, C. Sirlin, J. Simon, New Journal of Chemistry 11 (1987) 455–456.
[42] N. Suzuki, U. S. Patent Appl. Publ. 7056959 B2 (2004).
[43] M. Quintiliani, A. Kahnt, T. Wölfle, W. Hieringer, P. Vázquez, A. Görling, D.M. Guldi, T. Torres, Chemistry – A European Journal 14 (2008) 3765–3775.
[44] H. Uchida, H. Tanaka, H. Yoshiyama, P.Y. Reddy, S. Nakamura, T. Toru, Synlett 10 (2002) 1649–1652.
[45] R. Kenkyusho, Y. Akira, O. Yoshihito, Jap. Patent 61-207461A (1986).
[46] R. Kenkyusho, Y. Akira, O. Yoshihito, Jap. Patent 61-207431A (1986).
[47] M. Selcukoglu, E. Hamuryudan, Dyes and Pigments 74 (2007) 17–20.
[48] S. Wei, D. Huang, L. Li, Q. Meng, Dyes and Pigments 56 (2003) 1–6.
[49] I. Gürol, M. Durmuş, V. Ahsen, T. Nyokong, Dalton Transactions 34 (2007) 3782–3791.
[50] J. Battiste, R.A. Newmark, Progress in Nuclear Magnetic Resonance Spectroscopy 48 (2006) 1–23.
[51] O.E. Sielcken, M.M. Tilborg, M.F.M. Roks, R. Hendriks, W. Drenth, R.J.M. Nolte, Journal of the American Chemical Society 109 (1987) 4261–4265.
[52] H.J. Xu, G.X. Xiong, Journal of Photochemistry and Photobiology A 92 (1995) 35–38.
[53] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, 2nd ed., Pergamon Press, Oxford, 1989.
[54] J.G. Young, W. Onyebuagu, Journal of Organic Chemistry 55 (1990) 2155–2159.
[55] D. Wöhrle, M. Eskes, K. Shigehara, A. Yamada, Synthesis (1993) 194–196.