

Novel pyrazole functionalized phthalocyanines and their first row transition metal complexes†

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Pyrazole functionalized phthalodinitriles derived from 4,5-dichlorophthalonitrile by S^NAr reactions were used as precursors for the synthesis of phthalocyanines substituted with pyrazolyl groups in the 2,3,9,10,16,17,23,24-positions. The phthalocyanines were characterized by means of MALDI-TOF MS, IR, NMR and UV-Vis spectroscopy. The corresponding first row transition metal complexes with Mn(III), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) could be obtained by metal insertion and/or template synthesis.

Introduction

The development of new synthetic strategies for the synthesis of substituted phthalocyanines (PCs) is a constantly growing field of interest, since these molecules and their (transition) metal complexes have found application in different areas of research,¹ such as photoreceptors in photographic printing^{1b} or in photodynamic cancer therapy (PDT).² Zinc and aluminium phthalocyanines are used as photosensitizers, copper phthalocyanine is a commercially used blue printing dye.³ However, high-tech applications of phthalocyanines are somewhat restricted due to their special physical properties: the planar geometry of the phthalocyanine molecule gives rise to a remarkable high stability of π -aggregates, which are poorly soluble in almost every solvent. Further problems are directed to the phthalocyanine synthesis. Harsh reaction conditions are often required, which limit the choice of substituents at the aromatic backbone and lead to the formation of undesirable side products.

By introduction of substituents, the photochemical characteristics of phthalocyanines can be fine-tuned. As reported by Kobayashi and Luk'yanets *et al.* who evaluated the electronic effects of different substituents on the photochemical features of phthalocyanines by means of a computational analysis,⁴ the production of electron poor but well-soluble species would be of special interest.⁵ However, only a few examples of phthalocyanines functionalized with electron withdrawing substituents have been reported in the literature,⁶ most of them possessing simple moieties such as fluorine, chlorine or nitro substituents, which again give rise to a poor solubility of the products.

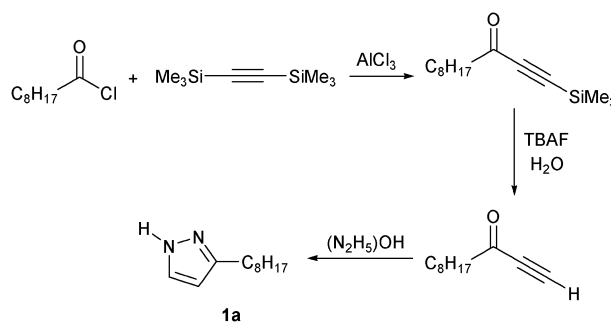
We have been working for a couple of years on the synthesis and the catalytic applications of pyrazol derived ligands and

found pyrazoles to be ideal candidates for the fine-tuning of steric and electronic ligand properties.⁷ Pyrazoles can be synthesized step-by-step from versatile precursor compounds, which allows a simple introduction of electron withdrawing or donating groups as well as of long alkyl side chains to overcome solubility problems. The pyrazolyl moiety itself is an electron withdrawing group, a property which can be enhanced by protonation or alkylation of both nitrogen atoms. To the best of our knowledge there is only one publication on pyrazole functionalized phthalocyanines in the literature: in 1996 Llamas-Saiz *et al.* reported the synthesis of a hexadecapyrazolyl substituted phthalocyanine.⁸ One further article was published on an octatriazolyl functionalized phthalocyanine.⁹

In the present paper we report the synthesis of a series of novel octasubstituted phthalocyanines bearing modified pyrazoles in the 2,3,9,10,16,17,23,24-positions. The usage of 3-octyl- and 3-*tert*-butylpyrazole as precursors leads to well-soluble phthalocyanines, which allows us to obtain NMR spectra for structural characterization.

Results and discussion

Due to its two nitrile groups, 4,5-dichlorophthalodinitrile (**2**) readily undergoes S^NAr reactions when treated with appropriate nucleophiles. For this purpose we used the pyrazoles **1a** and **1b**, functionalized in the 3-position. The 3-octyl derivative **1a** is accessible *via* an alkynone (Scheme 1).¹⁰ Elguero *et al.* reported the synthesis of 3-*tert*-butylpyrazole (**1b**).¹¹ The

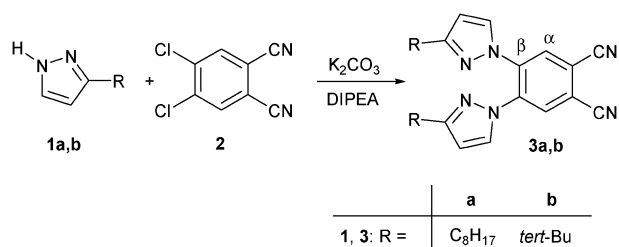


Scheme 1 Synthesis of 3-octylpyrazole **1a**.

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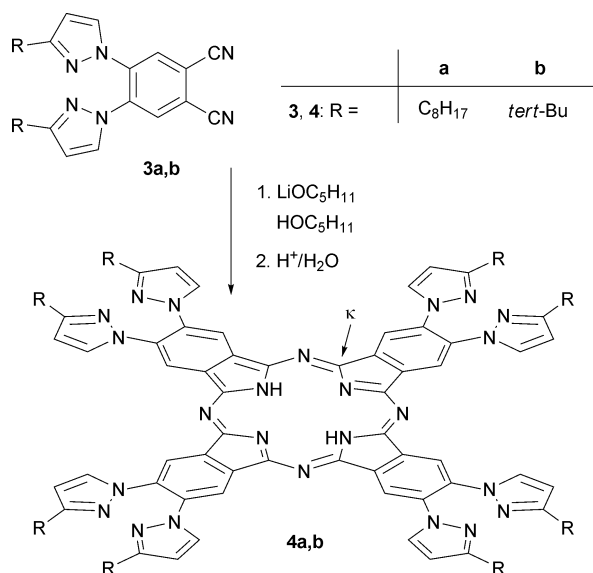
Scheme 2 Formation of the 4,5-disubstituted phthalodinitriles **3a** and **b** by S^NAr reactions.

synthesis of 4,5-dipyrzole functionalized phthalodinitriles, used as starting materials for the phthalocyanines, relies on a procedure published by Wöhrle *et al.* They reported a route leading to 4,5-dichlorophthalodinitrile (**2**) starting from commercially available 4,5-dichlorophthalic acid in just four steps with an overall yield of 60%.¹²

Heating the precursors **1a** or **1b** with 4,5-dichlorophthalodinitrile (**2**) in DMSO in the presence of K_2CO_3 and DIPEA (*N,N*-diisopropylethylamine) gave the 4,5-difunctionalized phthalodinitriles **3a** and **b**, respectively (Scheme 2).¹³

In all cases the nucleophilic attack of the pyrazoles occurred exclusively by the sterically less hindered nitrogen atom in 1-position. The resulting difunctionalized phthalodinitriles **3a** and **b** are well soluble in organic solvents, which allowed NMR spectroscopic characterization. Due to the electron withdrawing character of the four substituents at the aromatic ring, the proton H_α is observed in the 1H NMR spectra at about 8.20 ppm. The infrared spectra of the phthalodinitriles show strong absorptions at approximately 2230 cm^{-1} , which are assigned to the $C\equiv N$ stretching vibrations of the nitrile groups.

Heating of **3a** and **b** in *n*-pentanol in the presence of lithium pentanolate¹⁴ followed by hydrolysis of the intermediate lithium salts in diluted HCl gave the 2,3,9,10,16,17,23,24-octapyrazolyl



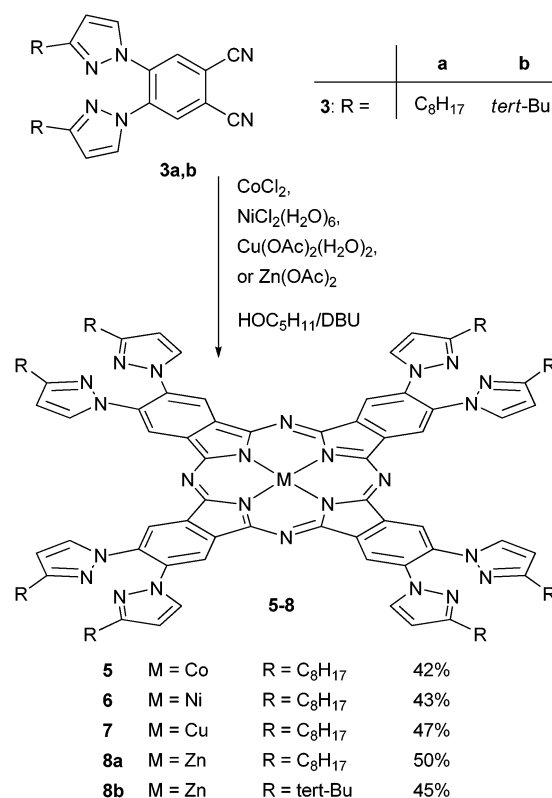
Scheme 3 Synthesis of the octapyrazolyl functionalized phthalocyanines **4a** and **b**.

functionalized phthalocyanines **4a** and **b** in yields of 39% (**4a**) and 41% (**4b**) (Scheme 3).

Due to the aliphatic substituents at the pyrazolyl moieties, **4a** and **b** are well soluble in chlorinated hydrocarbons. According to the ring current the resonances of the protons next to the pyrazole substituents appear at around 9.3 ppm in the 1H NMR spectra. This chemical shift is comparable to the data of other phthalocyanines functionalized with electron withdrawing substituents such as 2,3,9,10,16,17,23,24-octafluoro- and 2,3,9,10,16,17,23,24-octanitrophthalocyanine.¹⁵ In contrast to **4a**, the 1H NMR resonances of **4b** are strongly broadened, which we explain by aggregation supported by hydrophobic interactions. It seems that the more flexible octyl chains in **4a** suppress the intermolecular aggregation more efficiently than the rigid *tert*-butyl groups in **4b**. Interestingly the carbon atoms κ give a quite broad signal (see ESI†), due to tautomerism of the NH groups.

Co(II), Ni(II), Cu(II) and Zn(II) phthalocyanines were prepared by following a template strategy¹⁶ with the phthalodinitriles **3a** and **b** as starting material. An appropriate metal salt and the phthalodinitrile were dissolved in *n*-pentanol in the presence of the strong, non-coordinating organic base 1,9-diazabicyclo[5.4.0]undec-7-ene (DBU) and heated for several days. Finally the solvent was removed and the residue purified by standard techniques giving the complexes in yields of about 40–50% (Scheme 4).

Compounds **5–8** are again soluble in organic solvents, showing 1H NMR spectra with considerably broadened resonances, a feature that can be traced back to intermolecular



Scheme 4 Synthesis of the transition metal phthalocyanine complexes **5–8**.

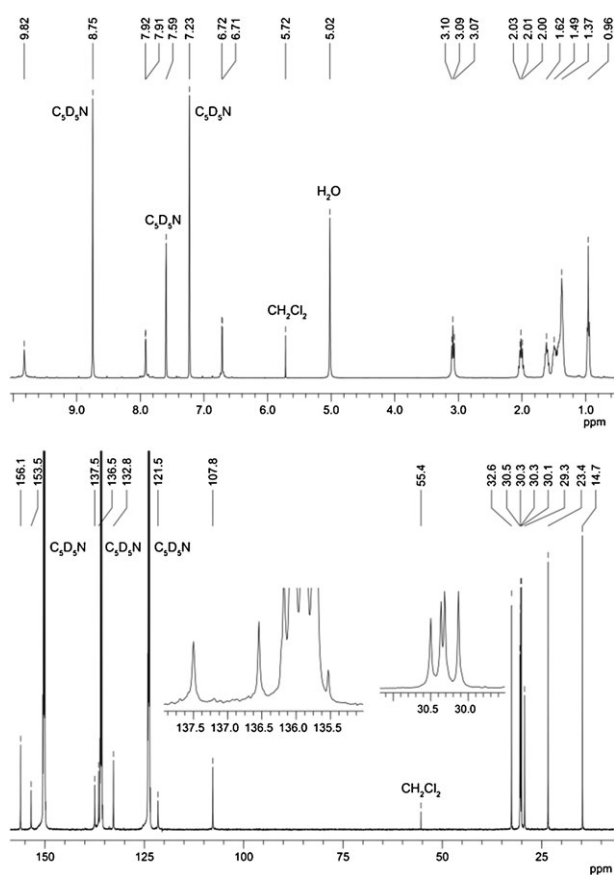
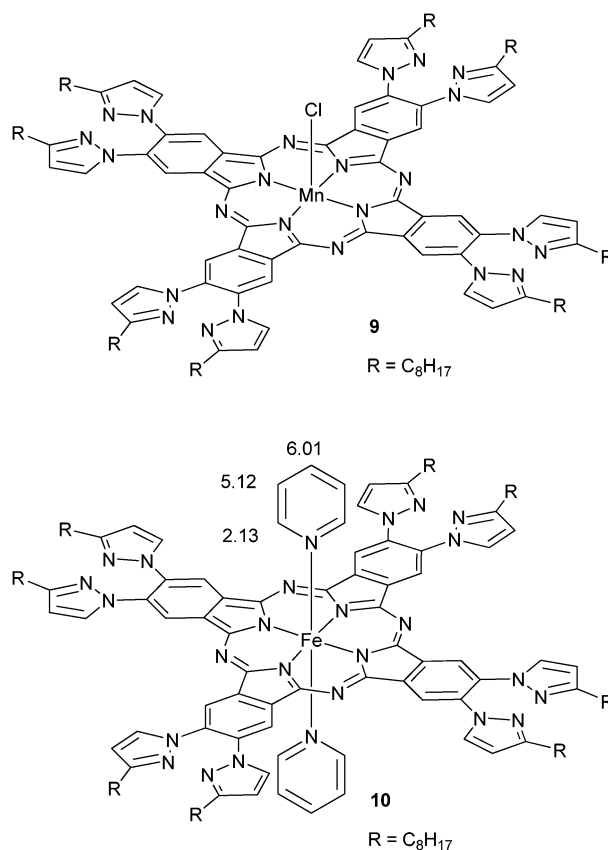


Fig. 1 ^1H NMR (top) and ^{13}C NMR spectra (bottom) of the zinc phthalocyanine complex **8a** ($\text{C}_5\text{D}_5\text{N}$).

aggregation and to the paramagnetic nature of the complexes (in the case of **5** and **7**). For the nickel complex **6** it was even impossible to obtain any acceptable NMR spectrum at all. This special behavior of nickel phthalocyanines is known from the literature.¹⁷ The zinc complexes **8a** and **b** gave sharp NMR signals after the addition of pyridine or by carrying out the NMR experiment in neat $\text{C}_5\text{D}_5\text{N}$ (Fig. 1). Zinc phthalocyanines undergo coordination of pyridine in the axial position, which efficiently suppresses intermolecular aggregation in solution.

Starting from the phthalocyanine **4a** it was possible to obtain the corresponding Mn(III) and Fe(II) complexes **9** and **10** by direct introduction of the metal ions (Scheme 5). The manganese(III) phthalocyanine **9** was obtained in 64% yield by heating a solution of $\text{Mn}(\text{OAc})_2(\text{H}_2\text{O})_4$ and **4a** to 100 °C in a mixture of dodecane and DMF in the presence of air for several hours. The iron(II) complex **10** was prepared in 76% yield according to a procedure published by Kobayashi *et al.*¹⁸ reacting $\text{FeCl}_2(\text{H}_2\text{O})_4$ and **4a** in refluxing pyridine. The resulting six coordinate low spin iron(II) complex is stabilized by two axially coordinated pyridine ligands. Due to the ring current of the chelating 18e phthalocyanine ligand, the resonances of the pyridine protons are shifted to a higher field, depending on the distance between the proton and the phthalocyanine ring: *e.g.* resonances of the protons in the *ortho*-positions of the coordinated pyridine ligands appear at a chemical shift of 2.13 ppm (Fig. 2). The HMQC spectrum



Scheme 5 Molecular structures of the phthalocyanine complexes **9** and **10** and the chemical shifts of the pyridine protons (ppm).

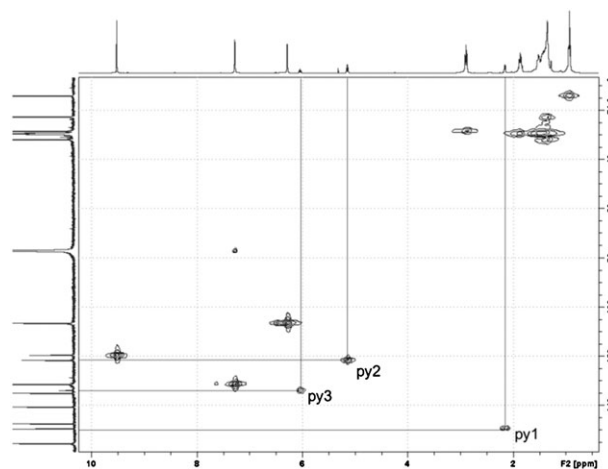


Fig. 2 ^1H - ^{13}C HMQC NMR spectrum of compound **10** (CDCl_3).

additionally allowed us to assign the resonances of the alkyl chain as well as the signals of the aromatic carbon atoms.

A further proof of the molecular structure of the phthalocyanines and their transition metal complexes resulted from MALDI-TOF mass spectrometry. Exemplary, the mass spectrum of phthalocyanine **4a** is shown in Fig. 3. There is a small deviation between the simulated and the detected isotope pattern for this compound. The observed pattern results from an overlay of two signals. The major component is the protonated molecule $\text{M} + \text{H}^+$, which proves the high proton

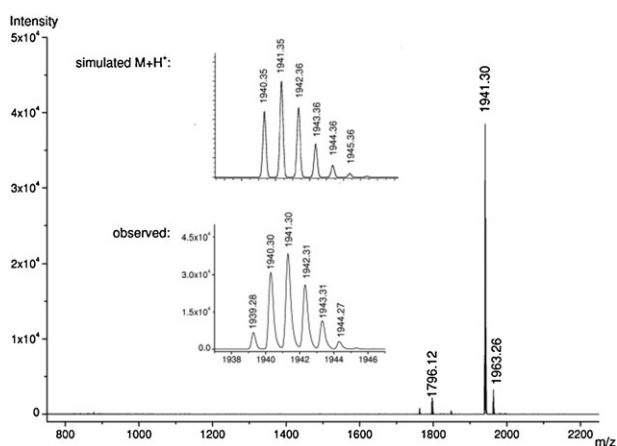


Fig. 3 MALDI-TOF mass spectrum of compound **4a**; the insets show the isotope patterns for the dominant peak, top: simulated, bottom: observed.

affinity of the pyrazole substituents and the minor component is the radical cation $M^{\bullet+}$.

The phthalocyanines **4a** and **b** and the transition metal complexes **5–10** were investigated by means of UV-Vis spectroscopy. Fig. 4 shows the absorption spectra of **4a** and **8a** for comparison. Pyrazole substituted phthalocyanines generally exhibit a red-shifted Q-band compared to the unfunctionalized phthalocyanine $H_2C_{32}H_{16}N_8$. A comprehensive examination on the influence of substituents in the α - and β -position (see Scheme 2) on the Q-band was reported by Kobayashi and Luk'yanets *et al.*⁴ According to their results a red shift of the Q-band is indicative of an electron withdrawing substituent in the β -position. Due to the lower symmetry of metal-free phthalocyanine compared to metal containing systems, compound **4a** shows a split Q-band.

The influence of the metal atom on the position of the Q-band is illustrated in Fig. 5; it is already visible to the naked eye for the dissolved compounds. The manganese compound **9** exhibits a yellow color, while the cobalt complex **5** is of deep blue color. Complex **9** turns out to give the largest red shift of all prepared phthalocyanines with a Q-band at 746 nm. Untypical for most phthalocyanines, the iron complex **10**

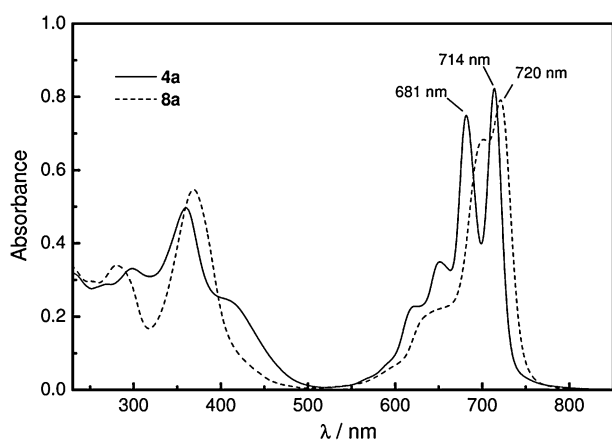


Fig. 4 UV-Vis absorption spectra (CH_2Cl_2) of the free phthalocyanine **4a** and its zinc complex **8a**.

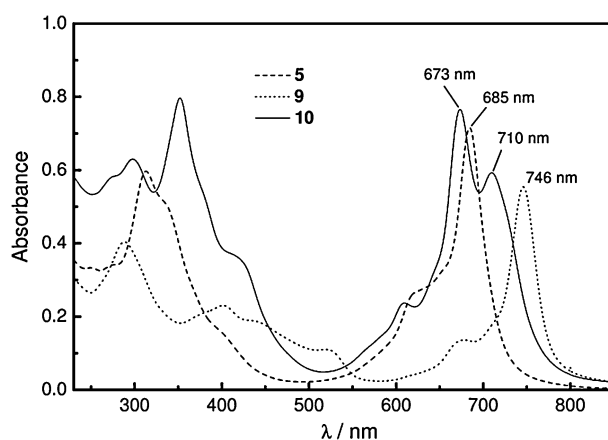


Fig. 5 UV-Vis absorption spectra (CH_2Cl_2) of the phthalocyanine complexes **5**, **9** and **10**.

exhibits a very strong Soret band, which is even more intense than its Q-band. The shoulder at 422 nm in the UV-Vis spectrum of **10** can be assigned to a MLCT transition which is typical for iron(II) low spin phthalocyanines.¹⁹ Compound **10** and to some extent also compound **8a** show a splitting of the Q-bands. This may be due to the formation of dimers as reported by Kobuke *et al.*, who observed a similar behavior for imidazolyl functionalized zinc phthalocyanine systems.²⁰

Conclusions

A series of octapyrazol substituted phthalocyanines and derived first row transition metal complexes were synthesized and characterized. The route shown here opens up a new and efficient way to a multitude of novel phthalocyanines functionalized with electron withdrawing nitrogen substituents. Pyrazoles are simple to be varied in their steric and electronic properties, and thus will allow us to fine-tune the optical properties of the corresponding phthalocyanines. All pyrazole functionalized phthalocyanines exhibit a pronounced red shift of the Q-Band, especially the manganese complex **9**, suggesting potential applications in photodynamic therapy.

Experimental section

General remarks

All manipulations were performed under argon or nitrogen by using standard Schlenk technique unless otherwise specified. Solvents were dried by standard methods. Reagents were purchased and used without further purification, unless otherwise noted.

Characterization techniques

NMR spectra were recorded with a Bruker Avance 400 or 600 spectrometer. The infrared spectra (KBr, film) were recorded using a Jasco FT/IR-6100 spectrometer in a frequency range between 4000–400 cm^{-1} . MALDI-TOF mass spectra were examined with a Bruker ultraflex mass spectrometer with α -cyano-4-hydroxycinnamic acid as the matrix. UV-Vis spectra were measured with a Varian Cary 5000 spectrometer with CH_2Cl_2 as solvent.

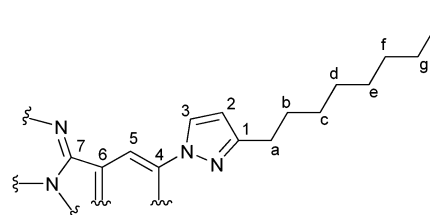
3-Octylpyrazole (1a). 8.05 g of bis(trimethylsilyl)acetylene (47.2 mmol) were slowly added to a cooled solution (0 °C) of 8.05 g of nonanoyl chloride (45.6 mmol) in 250 mL of absolute dichloromethane. The mixture was kept at 0 °C for 10 min, followed by the addition of 12.07 g of AlCl₃ (90.5 mmol) over a period of 2.5 h. The red mixture was stirred for one additional hour and after this time it was poured onto 300 mL of cooled 0.6 M HCl. The organic layer was separated and the aqueous layer was extracted with diethyl ether. The unified organic layers were dried over MgSO₄. After filtration, the solvent was removed under reduced pressure. The residue was again dissolved in 100 mL ether. A mixture of 1.98 g of NaF (47.2 mmol) and 1.32 g of TBAF (5.86 mmol) in 60 mL water was added to this solution and the resulting mixture was stirred for 12 h at rt. The layers were separated and the aqueous phase was extracted with diethyl ether. The unified organic phases were dried over MgSO₄ and the solvent was removed under reduced pressure, yielding a red oil. This oil was dissolved in 50 mL ethanol and cooled to -10 °C. 11 mL of N₂H₅OH (227 mmol) were added to this solution over a period of 1 h. After the addition was completed, the mixture was stirred for 12 h at rt. The solvent was removed and the residue distilled (90–120 °C, 10⁻² mbar), to give 5.67 g of **1a** (69%) as a pale yellow oil. IR (film, cm⁻¹): 3189 s, 3015 s, 2926 vs, 2855 vs, 1579 w, 1467 m, 1375 m, 1207 w, 1111 m, 1049 m, 1016 w, 937 m, 870 m, 767 m, 723 w, 614 w. ¹H NMR (CDCl₃, 400.13 MHz): δ = 0.86–0.89 (m, 3H, H-h), 1.27–1.31 (m, 10H, H-g–H-c), 1.63–1.70 (m, 2H, H-b), 2.66–2.70 (m, 2H, H-a), 6.08–6.22 (s, 1H, H-2), 7.49–7.50 (m, 1H, H-3), 10.47 (br s, 1H, NH). ¹³C NMR (CDCl₃, 150.92 MHz): δ = 14.2 (C-h), 22.8 (C-g), 26.8 (C-f), 29.3 (C-e), 29.4 (C-d), 29.5 (C-c), 29.6 (C-b), 32.0 (C-a), 103.5 (C-2), 135.2 (C-3), 148.0 (C-1).

4,5-Bis(3-octylpyrazol-1-yl)phthalodinitrile (3a). 1.60 g of **1** (8.12 mmol) and 2.93 g of **2a** (16.3 mmol) were dissolved in 20 mL of absolute DMSO under a nitrogen atmosphere and under protection from light. The mixture was stirred at 90 °C for 20 min. 2.8 mL of *N,N*-diisopropylethylamine (16.5 mmol) were added to this solution and the resulting mixture was stirred for 10 min, followed by the addition of K₂CO₃ in 12 portions of 0.8 g (5.79 mmol) in periods of 4 min. After this, the resulting dark solution was stirred at 110 °C for 1 h. The mixture was poured onto 100 g of ice and filtered. The solid residue was dissolved in 20 mL acetone and the product was reprecipitated by the addition of 25 mL water. The green solid was filtered off and dried under reduced pressure to give 1.49 g of **3a** (38%). The compound was stored under protection from light and under an inert gas atmosphere. IR (KBr, cm⁻¹): 3167 w, 3142 w, 2952 m, 2919 vs, 2850 vs, 2234 m, 1730 w, 1607 m, 1566 s, 1542 m, 1530 m, 1500 s, 1463 m, 1438 m, 1402 m, 1377 m, 1353 w, 1319 w, 1287 m, 1257 w, 1218 w, 1100 w, 1059 m, 1037 m, 999 w, 983 w, 945 m, 904 m, 871 w, 772 w, 756 m, 723 w, 556 w, 539 w, 507 w, 486 w, 440 w, 420 w. ¹H NMR (CDCl₃, 600.13 MHz): δ = 0.86–0.89 (m, 6H, H-h), 1.27–1.37 (m, 20H, H-g–H-c), 1.65–1.70 (m, 4H, H-b), 2.67–2.69 (m, 4H, H-a), 6.21–6.22 (d, ³J_{H,H} = 2.5 Hz, 2H, H-2), 6.87 (d, ³J_{H,H} = 2.5 Hz, 2H, H-3), 8.19 (s, 2H, H-5). ¹³C NMR (CDCl₃, 150.92 MHz): δ = 14.3 (C-h), 22.8 (C-g), 28.3 (C-f), 29.3 (C-e), 29.4 (C-d), 29.5 (C-c, C-b), 32.0 (C-a), 109.0

(C-2), 114.5 (C-6, C-7), 131.1 (C-5), 132.0 (C-3), 136.6 (C-4), 157.8 (C-1).

4,5-Bis(3-*tert*-butylpyrazole-1-yl)phthalodinitrile (3b). The synthesis of **3b** was accomplished according to the procedure described above. 1.20 g of **3b** (39%) were isolated as a colorless solid. The compound was stored under protection from light and under an inert gas atmosphere. IR (KBr, cm⁻¹): 3136 w, 2962 vs, 2903 m, 2866 m, 2233 m, 1606 s, 1565 vs, 1529 vs, 1509 s, 1480 w, 1455 s, 1402 w, 1374 vs, 1284 m, 1267 m, 1254 m, 1207 w, 1167 w, 1086 w, 1062 m, 1042 s, 992 m, 979 m, 950 s, 910 s, 874 w, 769 s, 723 w, 683 w, 665 w, 616 w, 535 w, 509 w, 487 w, 439 w. ¹H NMR (CDCl₃, 400.13 MHz): δ = 1.34 (s, 18H, H-b), 6.29 (d, ³J_{H,H} = 2.5 Hz, 2H, H-2), 6.85 (d, ³J_{H,H} = 2.5 Hz, 2H, H-3), 8.21 (s, 8H, H-5). ¹³C NMR (CDCl₃, 100.62 MHz): δ = 30.3 (C-b), 32.6 (C-a), 106.6 (C-2), 114.3 (C-6), 114.6 (C-7), 130.9 (C-5), 132.0 (C-3), 136.9 (C-4), 166.1 (C-1).

2,3,9,10,16,17,23,24-Octa(3-octylpyrazole-1-yl)phthalocyanine (4a). 140 mg of lithium (20.2 mmol) were dissolved in 5 mL degassed *n*-pentanol under an atmosphere of argon. 300 mg of **3a** (0.619 mmol) were added and the mixture was heated at 150 °C for 48 h. After this time, the solvent was removed and the residue was dissolved in 40 mL dichloromethane. The solution was treated with 35 mL of 0.1 M HCl, the phases were separated and the aqueous phase was discarded. This procedure was repeated twice. The green organic layer was washed three times with 40 mL water, dried over MgSO₄ and the solvent was removed under reduced pressure. The green solid was redissolved in dichloromethane and precipitated by the addition of acetone. This procedure was also repeated twice. The raw product was subsequently washed with 5 mL ethanol, 5 mL dimethylsulfoxide, 5 mL water, 5 mL acetone and 5 mL acetonitrile and dried in vacuum at 100 °C to yield 104 mg (35%) **4a** as a green solid. IR (KBr, cm⁻¹): 3290 w, 2955 s, 2923 vs, 2853 s, 1619 w, 1531 s, 1481 m, 1378 m, 1313 m, 1111 m, 1047 s, 1015 m, 949 m, 896 m, 753 s, 722 w, 687 w, 527 w. ¹H NMR (CDCl₃, 400.13 MHz): δ = 0.92–0.96 (m, 24H, H-h), 1.36–1.53 (m, 80H, H-g–H-c), 1.80–1.88 (m, 16H, H-b), 2.86–2.90 (m, 16H, H-a), 6.32 (m, 8H, H-2), 7.36 (s, 8H, H-3), 9.32 (br s, 8H, H-5). ¹³C NMR (CDCl₃, 150.92 MHz): δ = 14.3 (C-h), 22.9 (C-g), 28.7 (C-f), 29.6 (C-e), 29.7 (C-d), 29.9 (C-c), 30.0 (C-b), 32.2 (C-a), 107.0 (C-2), 121.1 (C-5), 132.1 (C-3), 134.4 (C-4), 136.1 (C-6), 148.5 (C-7), 156.0 (C-1). MALDI-TOF MS (*m/z*) 1941.3 (M + H⁺) (Scheme 6).



Scheme 6 Assignment of the NMR spectra for **4–10**.

2,3,9,10,16,17,23,24-Octa(3-*tert*-butylpyrazol-1-yl)phthalocyanine (4b). **4b** was synthesized similar to **4a** starting with 60 mg of lithium (8.64 mmol), 7 mL of degassed *n*-pentanol

and 300 mg of **3b** (0.815 mmol). The reaction proceeded for 24 h at 150 °C. The work-up procedure was similar to **4a**. Yield: 123 mg of **4b** (41%), green solid. IR (KBr, cm^{-1}): 3294 w, 2959 vs, 2927 w, 2902 w, 2865 w, 1623 m, 1530 vs, 1437 s, 1365 s, 1317 w, 1254 m, 1206 w, 1163 w, 1109 m, 1068 m, 1041 s, 1017 s, 980 w, 950 m, 895 m, 756 s, 723 w, 683 w, 647 w, 433 w. ^1H NMR (CDCl_3 , 600.13 MHz): δ = 1.49 (s, 72H, H-b), 6.38 (s, 8H, H-2), 7.44 (s, 8H, H-3), 9.25 (s, 8H, H-5). ^{13}C NMR (CDCl_3 , 150.92 MHz): δ = 30.8 (C-b), 32.6 (C-a), 104.8 (C-2), 121.2 (C-5), 131.5 (C-3), 134.6 (C-4), 136.6 (C-6), 149.0 (C-7), 164.3 (C-1). MALDI-TOF MS (m/z) 1492.7 ($\text{M} + \text{H}^+$).

[2,3,9,10,16,17,23,24-Octa(3-octylpyrazole-1-yl)phthalocyaninato]cobalt(II) (5). 20.1 mg of CoCl_2 (0.16 mmol), 300 mg of **3a** (0.16 mmol) and 0.3 mL of DBU (2.01 mmol) were dissolved in 4 mL *n*-pentanol and the mixture was stirred at 150 °C for 48 h. After this period, the solvent was removed in vacuum and the residue was dissolved in dichloromethane (25 mL). The solution was washed three times with 10 mL of water, the organic phase was dried over MgSO_4 , filtered and the solvent was removed under reduced pressure. The resulting black solid was two times redissolved in 25 mL dichloromethane and precipitated by the addition of acetone. This procedure was repeated two times with acetonitrile instead of acetone. After removal of the solvent, the product was washed with 5 mL ethanol, 5 mL dimethylsulfoxide, 5 mL water, 5 mL acetone and 5 mL acetonitrile and dried in vacuum to yield 130 mg of **5** (42%) as a dark blue solid. IR (KBr, cm^{-1}): 2923 vs, 2853 s, 2361 w, 1622 m, 1531 vs, 1482 s, 1378 m, 1320 m, 1116 s, 1045 m, 952 w, 917 w, 896 w, 781 w, 753 s, 496 w, 474 w, 459 w, 448 w, 431 w. MALDI-TOF MS (m/z) 1998.0 ($\text{M} + \text{H}^+$).

[2,3,9,10,16,17,23,24-Octa(3-octylpyrazole-1-yl)phthalocyaninato]nickel(II) (6). **6** was synthesized similar to **5** starting with 36.8 mg of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.16 mmol), 300 mg of **3a** (0.16 mmol) and 0.3 mL of DBU (2.01 mmol) in 4 mL *n*-pentanol. The reaction proceeded for 96 h at 150 °C. The work-up procedure was similar to **5**. Yield: 129 mg of **6** (42%), dark green solid. IR (KBr, cm^{-1}): 2954 s, 2923 vs, 2853 s, 1617 m, 1534 vs, 1484 s, 1465 s, 1377 s, 1319 m, 1224 w, 1113 s, 1044 s, 950 m, 918 m, 895 m, 751 s, 472 w. MALDI-TOF MS (m/z) 1997.6 ($\text{M} + \text{H}^+$).

[2,3,9,10,16,17,23,24-Octa(3-octylpyrazole-1-yl)phthalocyaninato]copper(II) (7). **7** was synthesized similar to **5** starting with 35.2 mg of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.18 mmol), 300 mg of **3a** (0.16 mmol) and 0.3 mL of DBU (2.01 mmol) in 4 mL *n*-pentanol. The reaction proceeded for 48 h at 150 °C. The work-up procedure was similar to **5**. Yield: 146 mg of **7** (47%), dark green solid. IR (KBr, cm^{-1}): 3102 w, 2955 s, 2923 vs, 2853 s, 1618 m, 1533 vs, 1509 m, 1481 s, 1432 s, 1378 m, 1343 m, 1319 m, 1228 w, 1115 m, 1043 m, 950 m, 909 m, 898, 779 m, 747 s, 703 w, 480 w, 405 w. MALDI-TOF MS (m/z) 2003.2 ($\text{M} + \text{H}^+$).

[2,3,9,10,16,17,23,24-Octa(3-octylpyrazole-1-yl)phthalocyaninato]zinc(II) (8a). **8a** was synthesized similar to **5** starting with 28.4 mg of $\text{Zn}(\text{OAc})_2$ (0.16 mmol), 300 mg of **3a** (0.16 mmol) and 0.3 mL of DBU (2.01 mmol) in 4 mL *n*-pentanol. The reaction proceeded for 96 h at 150 °C. The work-up procedure

was similar to **5**. Yield: 141 mg of **8a** (45%), dark green solid. IR (KBr, cm^{-1}): 2954 s, 2923 vs, 2853 s, 1620 w, 1531 vs, 1494 s, 1466 s, 1378 m, 1336 m, 1227 w, 1099 m, 1051 m, 992 w, 951 m, 902 m, 777 m, 744 s, 699 m, 471 w, 415 w. ^1H NMR (CDCl_3 , 400.13 MHz): δ = 0.93–0.97 (m, 24H, H-h), 1.37–1.50 (m, 64H, H-g–H-d), 1.57–1.62 (m, 16H, H-c), 1.97–2.04 (m, 16H, H-b), 3.06–3.10 (m, 16H, H-a), 6.70 (m, 8H, H-2), 7.91 (m, 8H, H-3), 9.82 (br s, 8H, H-5). ^{13}C NMR (CDCl_3 , 150.92 MHz): δ = 14.7 (C-h), 23.4 (C-g), 29.3 (C-f), 30.1 (C-e), 30.2 (C-d), 30.3 (C-c), 30.5 (C-b), 32.6 (C-a), 107.8 (C-2), 121.5 (C-5), 132.8 (C-3), 136.5 (C-4), 137.4 (C-6), 153.5 (C-7), 156.1 (C-1). MALDI-TOF MS (m/z) 2004.1 ($\text{M} + \text{H}^+$).

[2,3,9,10,16,17,23,24-Octa(3-tert-butylpyrazole-1-yl)phthalocyaninato]zinc(II) (8b). **8b** was synthesized similar to **5** starting with 37.1 mg of $\text{Zn}(\text{OAc})_2$ (0.20 mmol), 300 mg of **3b** (0.20 mmol) and 0.3 mL of DBU (2.01 mmol) in 4 mL *n*-pentanol. The reaction proceeded for 24 h at 150 °C. The solvent was removed in vacuum and the resulting residue was dissolved in dichloromethane (25 mL). The solution was washed three times with 10 mL water, the organic phase was dried over MgSO_4 , filtered and the solvent was removed under reduced pressure. The black solid was redissolved in 25 mL dichloromethane and precipitated by the addition of acetone. This procedure was repeated five times. After removal of the solvent, the product was washed two times with 5 mL ethanol and dried in vacuum to yield 126 mg of **8b** (40%) as a green solid. IR (KBr, cm^{-1}): 3294 w, 2958 vs, 2928 s, 2902 s, 2865 m, 1733 w, 1716 w, 1698 s, 1620 m, 1528 vs, 1494 vs, 1420 w, 1365 s, 1336 m, 1252 s, 1206 w, 1165 w, 1102 s, 1066 s, 1043 s, 980 w, 953 m, 903 s, 775 m, 746 m, 723 w, 700 w, 641 w, 437 w. ^1H NMR (CDCl_3 , 600.13 MHz): δ = 1.64 (s, 72H, H-b), 6.66–6.67 (m, 8H, H-2), 7.82 (s, 8H, H-3), 9.79 (br s, 8H, H-5). ^{13}C NMR (CDCl_3 , 100.62 MHz): δ = 31.2 (C-b), 33.1 (C-a), 105.3 (C-2), 121.6 (C-5), 132.4 (C-3), 136.8 (C-4), 137.5 (C-6), 153.7 (C-7), 164.4 (C-1). MALDI-TOF MS (m/z) 1555.6 ($\text{M} + \text{H}^+$).

Chloro[2,3,9,10,16,17,23,24-octa(3-octylpyrazole-1-yl)phthalocyaninato]manganese(III) (9). 48.5 mg of **4a** (0.025 mmol) and 31.2 mg of $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.127 mmol) were suspended in a mixture of 2 mL dimethylformamide and 2 mL dodecane. The mixture was heated to 100 °C for 4 h. The solvent was removed under reduced pressure at elevated temperature and the residue was dissolved in 40 mL dichloromethane. This solution was stirred with 40 mL brine for 24 h. Then the organic layer was separated and the solvent was removed. The residue was redissolved in 10 mL dichloromethane and precipitated by the addition of acetone. This procedure was repeated twice. Finally, the product was dried in vacuum at 100 °C for several hours, to yield 32.6 mg of **9** (64%) as a brown solid. IR (KBr, cm^{-1}): 2954 s, 2923 vs, 2853 s, 2351 w, 1620 m, 1533 vs, 1505 m, 1481 s, 1451 m, 1378 m, 1334 m, 1096 s, 1066 m, 1041 m, 949 w, 911 m, 845 w, 778 m, 746 s, 705 w, 459 w. MALDI-TOF MS (m/z) 1993.2 ($\text{M} - \text{Cl}^-$).

[2,3,9,10,16,17,23,24-Octa(3-octylpyrazole-1-yl)phthalocyaninato]bispyridineiron(II) (10). 48 mg of **4a** (0.025 mmol) and 18.4 mg of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.093 mmol) were dissolved in 5 mL

absolute pyridine under an atmosphere of argon. The solution was stirred for 2 h under reflux and subsequently filtered over 10 g of alumina. The alumina was thoroughly washed with dichloromethane. The washing solution and the filtrate were combined and the solvent was removed under reduced pressure. The resulting black solid was dissolved in 20 mL dichloromethane and precipitated by the addition of acetone. This procedure was repeated twice. Finally, the product was dried in vacuum at 50 °C for several hours to yield 41.2 mg of **10** (76%) as a dark green solid. IR (KBr, cm^{-1}): 2959 s, 2923 vs, 2853 s, 1620 m, 1532 vs, 1480 s, 1464 s, 1378 m, 1318 m, 1261 vs, 1100 vs, 1038 vs, 950 w, 916 w, 897 w, 802 vs, 754 m, 703 w, 620 w 475 w, 461 w, 412 w. ^1H NMR (CDCl_3 , 400.13 MHz): δ = 0.88–0.92 (m, 24H, H-h), 1.32–1.52 (m, 80H, H-g–H-c), 1.80–1.87 (m, 16H, H-b), 2.12–2.14 (m, 4H, H-py1), 2.85–2.88 (m, 16H, H-a), 5.10–5.14 (m, 4H, H-py2), 6.00–6.03 (m, 2H, H-py3), 6.26 (d, $^3J_{\text{H,H}}$ = 2.2 Hz, 8H, H-2), 7.25 (d, $^3J_{\text{H,H}}$ = 2.2 Hz, 8H, H-3), 9.49 (s, 8H, H-5). ^{13}C NMR (CDCl_3 , 150.92 MHz): δ = 14.3 (C-h), 22.9 (C-g), 28.6 (C-f), 29.5 (C-e), 29.6 (C-d), 29.7 (C-c), 29.8 (C-b), 32.1 (C-a), 107.0 (C-2), 119.8 (C-5), 121.8 (C-py2), 131.7 (C-3), 134.1 (C-py3), 135.3 (C-4), 140.9 (C-6), 147.7 (C-7), 149.7 (C-py1), 155.7 (C-1). MALDI-TOF MS (m/z) 1994.1 ($\text{M}^+ - 2\text{py}$).

References

- (a) *Phthalocyanines: Properties and Applications*, ed. C. C. Leznoff, A. B. P. Lever, VCH Publishers, New York, 1989–1996, vol. 1–7; (b) N. B. McKeown, *Phthalocyanine Materials: Synthesis, Structure and Function*, Cambridge University Press, Cambridge, 1998; (c) H. Ali and J. E. van Lier, *Chem. Rev.*, 1999, **99**, 2379–2450; (d) D. Hohnholz, S. Steinbrecher and M. Hanack, *J. Mol. Struct.*, 2000, **521**, 231–237; (e) P. Gregory, *J. Porphyrins Phthalocyanines*, 2000, **4**, 432–437; (f) G. De la Torre, C. G. Claessens and T. Torres, *Eur. J. Org. Chem.*, 2000, 2821–2830; (g) S. Palacin, *Adv. Colloid Interface Sci.*, 2000, **87**, 165–181; (h) D. Wöhrle, *Macromol. Rapid Commun.*, 2001, **22**, 68–97; (i) C. G. Claessens, W. J. Blau, M. Cook, M. Hanack, R. J. M. Nolte, T. Torres and D. Wöhrle, *Monatsh. Chem.*, 2001, **132**, 3–11; (j) C. Alexiou and A. B. P. Lever, *Coord. Chem. Rev.*, 2001, **216–217**, 45–54.
- (a) R. K. Pandey, *J. Porphyrins Phthalocyanines*, 2000, **4**, 368–373; (b) T. J. Dougherty, *Photochem. Photobiol.*, 1993, **58**, 895–900; (c) R. K. Pandey, K. Ravindra, G. Zheng and A. Gang, *Photodynamic Therapy in Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith, R. Guilard, Academic Press, San Diego, 2000.
- (a) L. Gao and X. Qian, *J. Fluorine Chem.*, 2002, **113**, 161–165; (b) H. Zollinger and A. Iqbal, *Color Chemistry*, Helvetica Chimica, Acta Zürich, Wiley-VCH, Weinheim, 2003, 3rd edn, pp. 140–157.
- N. Kobayashi, H. Ogata, N. Nonaka and E. A. Luk'yanets, *Chem.–Eur. J.*, 2003, **9**, 5123–5134.
- (a) B. A. Bench, A. Beveridge, W. M. Sharman, G. J. Diebold, J. E. van Lier and S. M. Gorun, *Angew. Chem.*, 2002, **114**, 773–776 (*Angew. Chem., Int. Ed.*, 2002, **41**, 747–750); (b) S. P. Keizer, J. Mack, B. A. Bench, S. M. Gorun and M. J. Stillman, *J. Am. Chem. Soc.*, 2003, **125**, 7067–7085.
- (a) R. Venugopala Reddy, J. Keshavayya, B. E. Kumara Swamy, M. N. K. Harish, H. R. Mallikarjuna and B. S. Sherigara, *Dyes Pigm.*, 2008, **80**, 1–5; (b) K. R. Venugopala Reddy, M. N. K. Harish, M. H. Moinuddin Khan and J. Keshavayya, *J. Fluorine Chem.*, 2007, **128**, 1019–1025; (c) M. Shigemitsu, *Bull. Chem. Soc. Jpn.*, 1959, **32**, 691–693; (d) D. Wöhrle, G. Meyer and B. Wahl, *Makromol. Chem.*, 1980, **181**, 2127–2135; (e) M.-S. Liao, T. Kar, S. M. Gorun and S. Scheiner, *Inorg. Chem.*, 2004, **43**, 7151–7161; (f) H. Brinkmann, C. Kelting, S. Makarov, O. Tsaryova, G. Schnurpfeil, D. Wöhrle and D. Schlettwein, *Phys. Status Solidi A*, 2008, **205**, 409–420; (g) B. Tylleman, G. Gbabode, C. Amato, C. Buess-Herman, V. Lemaure, J. Cornil, R. Gómez Aspe, Y. H. Geerts and S. Sergeev, *Chem. Mater.*, 2009, **21**, 2789–2797; (h) A. de la Escosura, M. V. Martínez-Díaz, D. M. Guldi and T. Torres, *J. Am. Chem. Soc.*, 2006, **128**, 4112–4118.
- (a) W. R. Thiel and T. Priermeier, *Angew. Chem.*, 1995, **107**, 1870–1872 (*Angew. Chem., Int. Ed.*, 1995, **34**, 1737–1738); (b) W. R. Thiel and J. Eppinger, *Chem.–Eur. J.*, 1997, **3**, 696–705; (c) H. Glas, M. Spiegler and W. R. Thiel, *Eur. J. Inorg. Chem.*, 1998, 275–281; (d) M. Barz, H. Glas and W. R. Thiel, *Synthesis*, 1998, 1269–1273; (e) M. Barz, E. Herdtweck and W. R. Thiel, *Angew. Chem.*, 1998, **110**, 2380–2383 (*Angew. Chem., Int. Ed.*, 1998, **37**, 2262–2265); (f) A. Hroch, G. Gemmecker and W. R. Thiel, *Eur. J. Inorg. Chem.*, 2000, 1107–1114; (g) M. Jia and W. R. Thiel, *Chem. Commun.*, 2002, 2392–2393; (h) Y. Sun, A. Hienzsch, J. Grasser, E. Herdtweck and W. R. Thiel, *J. Organomet. Chem.*, 2006, **691**, 291–298; (i) S. Bergner, G. Wolmershäuser, H. Kelm and W. R. Thiel, *Inorg. Chim. Acta*, 2008, **361**, 2059–2069; (j) D. Zabel, A. Schubert, G. Wolmershäuser, R. L. Jones Jr and W. R. Thiel, *Eur. J. Inorg. Chem.*, 2008, 3648–3654; (k) T. Jozak, M. Fischer, J. Thiel, Y. Sun, H. Kelm and W. R. Thiel, *Eur. J. Org. Chem.*, 2009, 1445–1452.
- L. Llamas-Saiz, N. Jagerovic, I. Alkorta, J. Elguero and C. Fernandez-Castano, *New J. Chem.*, 1996, **20**, 1081–1086.
- M. Juríček, P. H. J. Kouwer, J. Rehák, J. Sly and A. E. Rowan, *J. Org. Chem.*, 2009, **74**, 21–25.
- (a) H. G. O. Becker, W. Berger, G. Domschke, E. Fanghänel, J. Faust, M. Fischer, F. Gentz, K. Gewald, R. Gluch, R. Mayer, K. Müller, D. Pavel, H. Schmidt, K. Schollberg, K. Schwetlick, E. Seiler, G. Zeppenfeld, R. Beckert, W. D. Habicher and P. Metz, *Organikum*, Wiley-VCH, Weinheim, 2004, p. 498, vol. 21; (b) D. R. M. Walton and F. Waugh, *J. Organomet. Chem.*, 1972, **37**, 45–56.
- J. Elguero, E. Gonzalez and R. Jacquier, *Bull. Soc. Chim. Fr.*, 1968, **2**, 707–713.
- D. Wöhrle, M. Eskes, K. Shigehara and A. Yamada, *Synthesis*, 1993, 194–198.
- C. Lothschütz, Diploma thesis, TU Kaiserslautern, 2007.
- T. Kimura, T. Suzuki, Y. Takaguchi, A. Yomogita, T. Wakahara and T. Akasaka, *Eur. J. Org. Chem.*, 2006, 1262–1270.
- (a) K. Reddy, V. Ramareddy and J. Keshavayya, *Turk. J. Chem.*, 2002, **26**, 573–580; (b) B. N. Achar and J. M. Bhandari, *Transition Met. Chem. (London)*, 1993, **18**, 423–426; (c) H. Uchida, H. Yoshiyama, P. Y. Reddy, S. Nakamura and T. Toru, *Synlett*, 2003, 2083–2085; (d) A. K. Debnath, S. Jiang, N. Strick, K. Lin, P. Haberfield and A. R. Neurath, *J. Med. Chem.*, 1994, **37**, 1099–1108; (e) D. Wöhrle and B. Wahl, *Tetrahedron Lett.*, 1979, **20**, 227–228; (f) S. Hiller, D. Schlettwein, N. R. Armstrong and D. Wöhrle, *J. Mater. Chem.*, 1998, **8**, 945–954.
- (a) F. Yüksel, A. G. Gürek, C. Lebrun and V. Ahsen, *New J. Chem.*, 2005, **29**, 726–732; (b) W. Liu, C.-H. Lee, H.-S. Chan, T. C. W. Mak and D. K. P. Ng, *Eur. J. Inorg. Chem.*, 2004, 286–292; (c) D. Tian, X. Hou, Y. Chang, F. Cong, H. Yu, X. Du and G. Du, *Synthesis*, 2005, 741–748; (d) B. Görlach, M. Dachtler, T. Glaser, K. Albert and M. Hanack, *Chem.–Eur. J.*, 2001, **7**, 2459–2465.
- M. Hanack, G. Schmied and M. Sommerauer, *Angew. Chem.*, 1993, **105**, 1540–1542 (*Angew. Chem., Int. Ed.*, 1993, **32**, 1422–1424).
- T. Fukuda, S. Homma and N. Kobayashi, *Chem. Commun.*, 2003, 1574–1575.
- E. A. Ough and M. J. Stillman, *Inorg. Chem.*, 1994, **33**, 573–583.
- K. Kameyama, M. Morisue, A. Satake and Y. Kobuke, *Angew. Chem.*, 2005, **117**, 4841–4844 (*Angew. Chem., Int. Ed.*, 2005, **44**, 4763–4766).