DOI: 10.1002/ejoc.200901237

New Versatile Strategy towards Zinc(II)-, Copper(II)- and Cobalt(II)-Metallated Thiophene/Porphyrin-Hybrids

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Keywords: Porphyrinoids / Ligand design / Hybrid monomers / UV/Vis spectroscopy / Cyclic voltammetry

A series of linear and lateral functionalised porphyrin–thiophene hybrid molecules was synthesised. Directly linked metal-free conjugates were synthesised by a successive bromination/cross-coupling sequence and transformed subsequently into zinc, copper and cobalt porphyrins. In the lateral connection mode, diverse strategies were necessary to obtain zinc and cobalt porphyrins, whereas the synthesis of the copper derivative followed an established route. All compounds were investigated by cyclic voltammetry. Within the series, the cobalt derivatives were exceptional because the cobalt porphyrin oxidation proved to be in competition with the thiophene oxidation. These results lead to a better understanding of the redox behaviour because such hybrid molecules consist of two independent redox centres. Furthermore, in the linear case, the absorption spectra clearly indicated an electronic influence of the thiophene periphery on the porphyrin, although conjugation is hindered strongly.

Introduction

Since Heeger, Shirakawa and McDiarmid established doped polyconjugated systems as intrinsic conducting materials in organic chemistry, researchers have studied many systems to develop OLED, OFET, photovoltaic and sensoric devices.[1] In this respect, thiophene-based oligomers and polymers proved to be very promising because a highly diversified chemistry exists to tailor their properties.[2] Thiophenes are also best suited to combine electronic properties with optical or redox properties of other functional compounds, such as crown ethers, fullerenes or porphyrins.[3] Especially, porphyrins are at the centre of interest, not only due to their (opto-)electronic behaviour, but also due to their metal centre, which can be modified easily.[4]

Porphyrin–thiophene hybrid systems can, in general, be divided into lateral and linear connected types according to Collis et al. and Wolf.[5] Representatives of the lateral type were described by Ballarin et al., Bäuerle et al. and Collis et al.[4d–4h,5b] Bäuerle's and Collis' group determined the photovoltaic and sensoric properties of the resulting polymers. Furthermore, the groups of Collis and Shimidzu described linearly connected hybrid systems.[5b,6] However, all groups used varying porphyrin cores and connection patterns at the *meso*- or β-positions of the porphyrin units, making the comparison of the strategies difficult. A general approach for the reliable and convenient assembly of thiophen/porphyrin structures does not exist so far.

We recently demonstrated for nickel(II) derivatives that the direct linear thiophene–porphyrin connection can be easily realised using a new synthetic strategy by successive bromination and cross-coupling reaction steps.[7] The main advantage comes from the assembly of the free base hybrid, which represents a good starting material for the incorporation of metals other than nickel. Here, we provide evidence for the validity of this proposal. Furthermore, we show new methods for the synthesis of lateral-bound copper(II), zinc(II) and cobalt(II) porphyrin–terthiophene hybrids. All compounds were subjected to electrochemical analysis and are discussed in respect of their absorption properties.

Results and Discussion

Syntheses

Incorporation of diverse metal centres into the linear thiophene–porphyrin hybrids **1**, **5** and **9** was accomplished by using the Adler–Longo method (Scheme 1).[8] The free-base porphyrins were heated either in *N*,*N*-dimethylformamide (DMF) or in a mixture of MeOH, $CHCl_3$ and tetrahydrofuran (THF) with the appropriate metal(II) acetate. It was not necessary to reflux the solution because these milder conditions of 60–80 °C proved to be better to avoid oxidative degradation of higher oligothiophenes. The pro-

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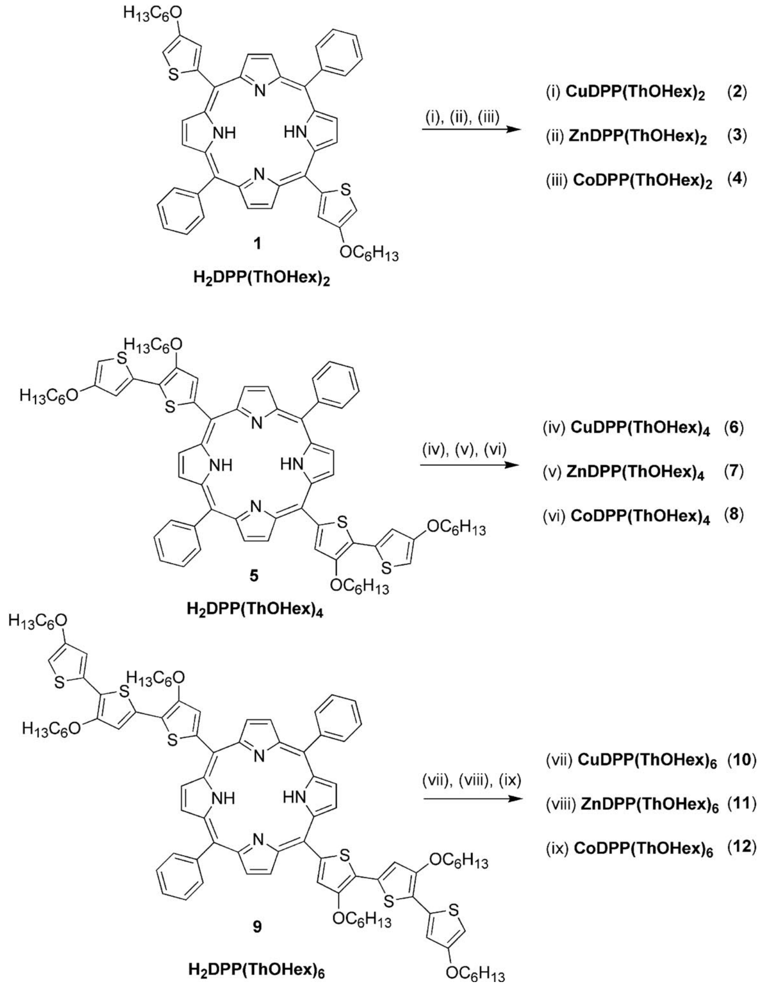
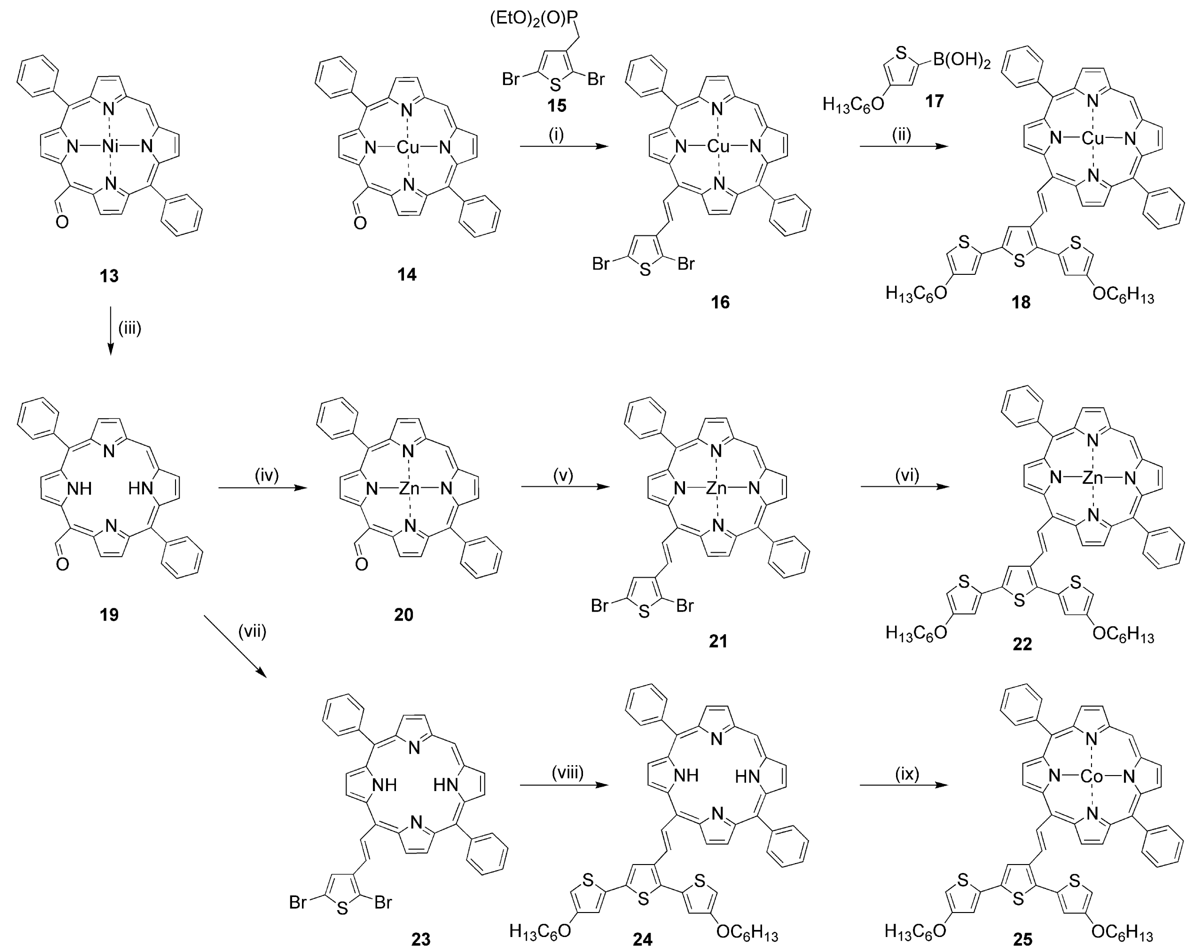
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.200901237.



Scheme 1. *Reagents and conditions*: (a) (i) $Cu(OAc)_2·H_2O$, $THF/CHCl_3/MeOH$, reflux, 1 h, 88%; (ii) $Zn(OAc)_2$, DMF, 60 °C, 1 h, 93%; (iii) $Co(OAc)_2·4H_2O$, DMF, reflux, 1 h, 79%; (iv) $Cu(OAc)_2·H_2O$, $THF/CHCl_3/MeOH$, reflux, 1 h, 90%; (v) $Zn(OAc)_2$, DMF, 140 °C, 1 h, 53%; (vi) $Co(OAc)_2·4H_2O$, DMF, 140 °C, 1 h, 76%; (vii) $Cu(OAc)_2·H_2O$, $THF/CHCl_3/MeOH$, reflux, 1 h, 68%; (viii) $Zn(OAc)_2$, DMF, 80 °C, 1 h, 53%; (ix) $Co(OAc)_2·4H_2O$, DMF, 80 °C, 1 h, 56%.

gress of the reaction could be monitored by thin layer chromatography (SiO_2; CH_2Cl_2/hexane mixtures) because the free bases gave streaky spots, whereas the metallated porphyrins were characterised by well-defined spots. For the thienyl **2**–**4** and bithienyl derivatives **6**–**8**, average yields of 80% were obtained. The terthienyls **10**–**12** were obtained in somewhat lower yields of 53–68% because more extensive purification steps involving column chromatography and/or crystallisation were required. In the case of zinc porphyrins **3**, **7** and **11**, generation of the metalloporphyrins was confirmed by ^1H NMR analysis, whereby the broad signals of the tautomeric NH protons at δ = –2.6 to –2.8 ppm disappeared. The paramagnetic copper and cobalt porphyrins **2**, **4**, **6**, **8**, **10** and **12** were identified by mass spectrometry. Whereas EI mass spectrometry was the most suitable technique for analysing the thienyl porphyrins **2**–**4**, ESI-MS or APCI-MS were necessary to detect the higher weight bisthienyl porphyrins **6**–**8** and terthienyl porphyrins **10**–**12**. Interestingly, ESI-MS produced not only the $[M + H]^+$ adduct ion, but also the $[M]^{+\cdot}$ ion, which can be attributed to the high voltage conditions and resulting oxidations.[9] APCI-MS gave only the $[M + H]^+$ adduct in most cases.

The synthesis of laterally connected porphyrin–thiophene hybrids started with a regioselective Vilsmeier formylation of (5,15-diphenylporphyrinato)nickel(II) at the *meso*-position, according to literature, to give **13**.[10] This reaction sequence could be adapted to the preparation of Cu-porphyrin **14** (Scheme 2).[11] Aldehyde **14** and phosphonate **15** were subjected to a Horner–Emmons reaction to give **16** in 74% yield. The configuration of the newly formed double bond could not be deduced with certainty from the ^1H NMR spectra. However, considering the reaction mechanism and the secure configuration of the analogous nickel and zinc-compounds, it is plausible that **16** is the *E* isomer. The dibromothiophene derivative **16** afforded terthiophene-connected porphyrin **18** by a Suzuki coupling with boronic acid **17** in 82% yield. The formation of both copper compounds were confirmed by EI mass spectrometry, which showed characteristic ions of 787 $[M]^{+\cdot}$, 707



Scheme 2. *Reagents and conditions*: (a) (i) **15**, NaH, DME, room temp., 22 h, 74%; (ii) **17**, Pd(PPh$_3$)$_4$, DME, 1 M Na$_2$CO$_3$, reflux, 3 h, 82%; (iii) concd. H$_2$SO$_4$/TFA, room temp., 30 min, 74%; (iv) Zn(OAc)$_2$, DMF, reflux, 3 h, 72%; (v) **15**, NaH, DME, room temp., 4 h, 70%; (vi) **17**, Pd(PPh$_3$)$_4$, DME, 1 M Na$_2$CO$_3$, reflux, 5 h, 64%; (vii) **15**, NaH, DME, reflux.

$[M^{+\cdot}-\mathrm{Br}]$ and 627 $[M^{+\cdot}-2\,\mathrm{Br}]$ for **16**, and 995 $[M]^{+\cdot}$ for **18**.

Because zinc porphyrin **20** was not available through direct formylation of (5,15-diphenylporphyrinato)zinc(II), its synthesis therefore started with the demetallation of **13** under acidic conditions.[11,12] The metal-free porphyrincarbaldehyde **19** was obtained in 74% yield. Subsequent zinc incorporation into **19** furnished **20** in 72% yield.[13] The terthiophene **22** was prepared similarly by a Horner–Emmons reaction, which gave 70% of **21**, and a subsequent Suzuki coupling in 64% yield. The formation of the *E* isomer was verified for both **21** and **22** by the coupling constants of J = 16.0 Hz and J = 15.8 Hz, respectively, for the vinylene protons.

The corresponding cobalt derivative is expected to be sensitive to oxidation and therefore difficult to purify by column chromatography. To circumvent these problems, a synthetic route involving the free base with incorporation of the cobalt as the last step was envisaged because the metallation process can often be performed without chromatography. A Horner–Emmons reaction with porphyrin **19** and phosphonate **17** yielded 60% of **23** as the pure *E* isomer (J = 16.0 Hz). In contrast to the all other Horner–Emmons reactions presented here, in this case the solution required heating to reflux. This can be rationalised on the basis that the free base macrocycle is more electron-poor compared to the dianionic species of metallated porphyrins. The following Suzuki coupling proceeded uneventfully to give terthiophene **24** in 82% yield. For insertion of the metal, **24** was heated to reflux with cobalt(II) acetate in DMF, according to the general Adler–Longo procedure.[8] The thiophene–porphyrin hybrid **25** was obtained in 61% yield and characterised by the high intensity ions of 991 $[M]^{+\cdot}$ in the ESI-MS and 992 $[M + H]^{+}$ in the APCI-MS.

Absorption Spectra

For all target compounds, the absorption spectra showed the typical bands for metallated porphyrins − one Soret band and two Q bands − that were indicative for successful metal insertion into the free base porphyrins.[14] Comparing the members with increasing thiophene chain lengths (**2/6/10**, **3/7/11** and **4/8/12**) within the linear connected thiophene–porphyrin hybrids series provided interesting results. For all the metal cores, not only did the α-band shift to the

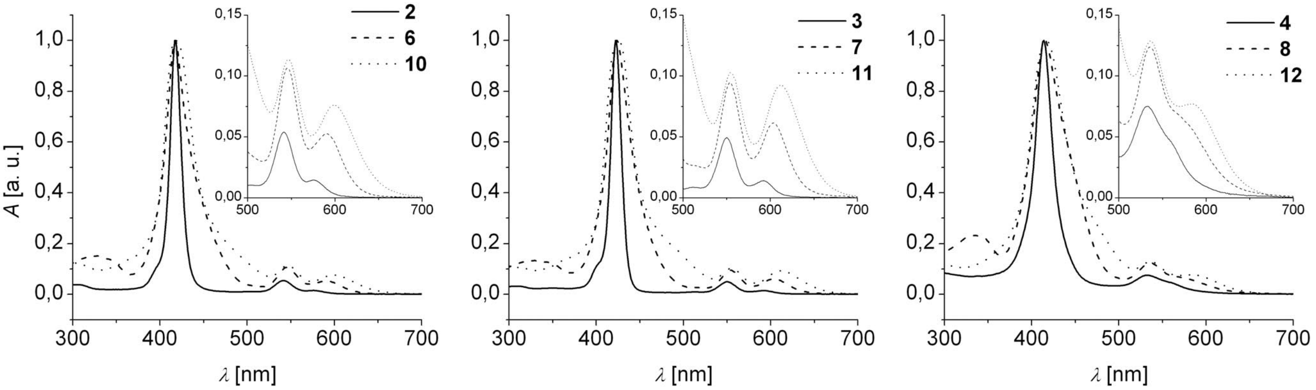


Figure 1. Absorption spectra of all linearly connected thiophene/porphyrin hybrids.

red due to the extension of the π-system, but the Soret band also broadened significantly without shifting its position (full width at half maximum, fwhm). At 10–20% of the maximum, this tendency was even more prominent. Furthermore, for the zinc and copper derivatives, the α-band intensity was raised compared to the β-band (Figure 1). Table 1 summarises all significant data.

Table 1. Details of the Soret-, α- and β-bands.

Compound	Metal	Soret band [nm]	fwhm [nm]	Absorption α/β
CuDPP[a]	Cu	403	11	1:3.6
2		418	15	1:3.9
6		417	35	1:2.0
10		418	40	1:1.5
ZnDPP[a]	Zn	407	11	1:7.8
3		422	15	1:3.5
7		423	34	1:1.5
11		425	37	1:1.1
CoDPP[a]	Co	398	17	1:1.8
4		414	25	1:1.5
8		415	53	1:1.8
12		417	53	1:1.7

[a] DPP = 5,15-diphenylporphyrin; the metallated porphyrins were used as references.

These observations can be explained by taking the Gouterman-Four-Orbital-Theory into account.[14] Gouterman describes two degenerated LUMOs, e_g, and two almost degenerate frontier orbitals, A_{1u} and A_{2u}; significantly, whereas the former frontier orbital includes a nodal plane at the *meso*-position, the second does not. Therefore, electron-donating effects would affect the A_{2u} orbital in particular. With regard to the correlation

$$A_\alpha/A_\beta \approx [\Delta E(A_{2u}, e_g) - \Delta E(A_{1u}, e_g)]^2$$

and provided that for 10,20-arylated 5,15-diphenylporphyrins the difference $\Delta E(A_{2u}, e_g) - \Delta E(A_{1u}, e_g)$ is negative, this means that electron-donating groups connected at the *meso*-position will raise the A_{2u} orbital, reduce the $\Delta E(A_{2u}, e_g)$ and therefore increase the α-band intensity.[15] Actually, the difference is described as negative for 5,10,15,20-tetraphenylporphyrins.[15,16] The conclusion that there is an electron-donating effect from the thiophene periphery towards the porphyrin can thus be drawn. This is more remarkable if one considers that conjugation between both aromatic systems is hindered due to steric repulsion.[17] A further hint supporting this conclusion was found in the broadened Soret band. The groups of Wolf, Röder and Odobel made similar observations concerning the Soret band and traced it back to the donating properties of the peripheral thiophene unit;[4j–4l,18] Rochford et al. describe similar effects for *meso*-substituted thien-2-ylzinc porphyrins.[19] Nonetheless, until now it has not been clear whether this effect is based on minimal conjugation or conjugation-independent redox processes, for example on a through-bond super-exchange mechanism.

Cyclic Voltammetry

Electropolymerisation offers many advantages compared to chemical polymerisation methods.[1b,20] When the resulting polymer is not soluble in organic solvents its processing may become difficult and, for such cases, electropolymerisation raises the possibility of depositing the polymer onto structured electrodes directly. Due to the anodic polymerisation mechanism, knowledge about the oxidation processes is fundamental and, in this respect, cyclic voltammetry is indispensable. Thereby, cyclic voltammetry experiments of linearly bound porphyrins gave interesting results (Figure 2). When the thiophene periphery was elongated from thienyl to terthiophenyl, the first oxidation peak, which was irreversible, shifted to lower potentials for the copper (**2**, **6** and **10**) and zinc (**3**, **7** and **11**) derivatives. The oxidation peaks were located at 1.12–1.19 V for the thiophene periphery, at 1.04–1.09 V for the bithiophenyls and at 0.86–0.88 V for the terthiophenyls. These results are in good agreement with the oxidation potentials reported for the analogous nickel complexes.[7] The first oxidation potential of the linearly connected cobalt porphyrins (**4** and **8**: 0.96 V) did not change for the thienyls and bithiophenyls. Furthermore, it showed reversible character, especially when the vertex potentials were reduced to lower values (see the Supporting Information for further CV experiments with **4**, **8** and **12**). An approximation to the cyclic voltam-

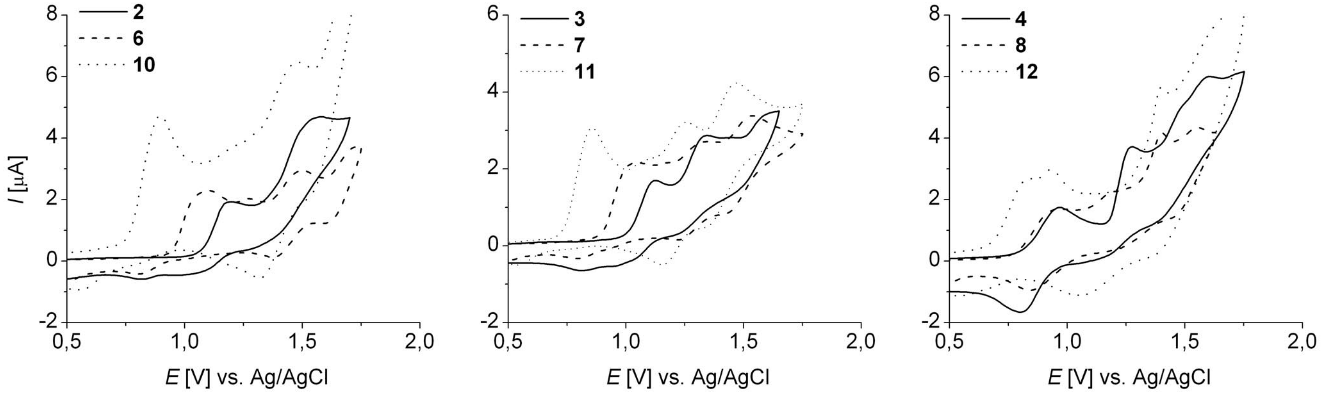


Figure 2. Cyclic voltammograms of the linearly connected thiophene/porphyrin hybrids.

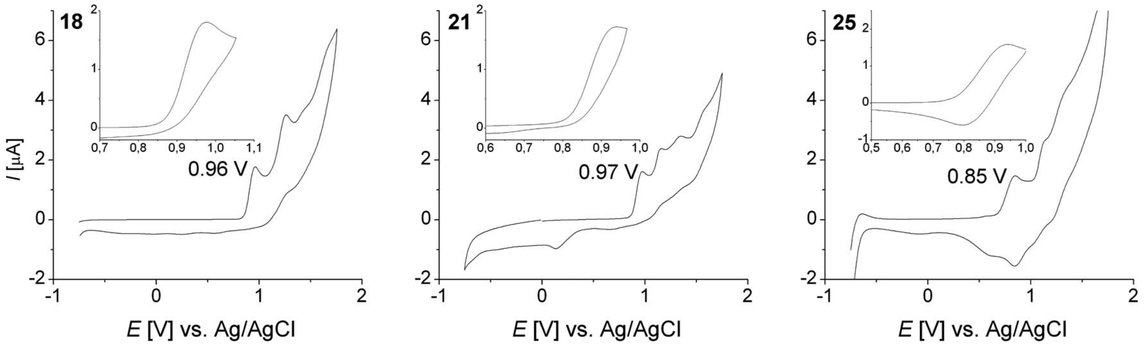


Figure 3. Cyclic voltammograms of the laterally connected thiophene/porphyrin hybrids.

metry behaviour of the other porphyrin complexes was not observed until the oligothiophene chain was a terthiophene (**12**). In this case the first oxidation wave was a double peaked signal with two maxima at 0.83 V and 0.93 V. The former peak corresponded to those of **10** and **11** and the latter can be attributed to a cobalt porphyrin oxidation process. The fact that the oxidation events of copper- and zinc-containing hybrids are fundamentally different to those of cobalt can be explained by comparison with the cyclic voltammograms of the analogous 5,15-diphenylporphyrins (DPP; see the Supporting Information). CoDPP has the lowest oxidation potential among them. Because the linearly connected thiophene–porphyrin hybrids consist of two almost independent redox units, the thiophene and porphyrin oxidations occur according to their ease of oxidation.[7] The irreversible thiophene oxidation is the first to occur in the case of copper and zinc porphyrins. For the cobalt complexes, the reversible cobalt porphyrin is most sensitive to oxidation. Only in the trishexoxyterthiophene-carrying cobalt complex is the thiophene unit more easily oxidised. The assignment of the peak at 0.93 V as an oxidation process at the cobalt porphyrin unit is strengthened by its reversible character, because irreversible electropolymerisation processes should occur when the thiophene was oxidised.[20f,20g] Whether the first cobalt porphyrin oxidation takes place at the π-system of the porphyrin or at is metal-centre is not yet clear. Kadish describes both in his very comprehensive review on the electrochemistry of metalloporhyrins.[21]

An exceptional role for cobalt porphyrins was even found in the lateral case (Figure 3). The copper and zinc complexes **18** and **21** showed the same irreversible first oxidation occurring at 0.96 V, which was comparable to that of the reported nickel derivative.[7] In contrast, cobalt porphyrin **25** was oxidised at a lower potential of 0.85 V; compared to **12**, this was slightly shifted to lower potentials due to the electron-donating effect of the vinyl-bonded terthiophene unit. The reversibility of the first oxidation event of **25** became clear when the vertex potentials were reduced to lower values (Figure 3, insets).

Conclusions

The results presented here show that the electrooxidation of thiophene–porphyrin hybrid systems is regiodefined and that the overall oxidation process is dependent on the behaviour of the individual units. For electropolymerisation, the following facts must be considered: Cobalt porphyrins differ especially from analogous nickel, copper and zinc complexes due to their low oxidation potential, which competes with the thiophene oxidation in most cases. For linearly connected thiophene–porphyrin units, a small degree of electronic communication between the thiophene and porphyrin units can be assumed. Thiophene acts as an electron donor, resulting in a remarkable broadening of the Soret band of the porphyrin and an increase in the α-band intensity. Only for cobalt complexes does the α-band seem to be unaffected, which underlines their exceptional role in the investigated series.

Experimental Section

General: Air- and moisture-sensitive reactions were carried out under nitrogen in flame-dried flasks. Anhydrous solvents were used as received. Reaction progress was monitored by thin layer chromatography on Polygram SIL G/UV_{254} plates (Macherey–Nagel). Silica gel 60M (Macherey–Nagel) was used for column chromatographic separations. Melting points were determined with a Stuart-Melting-Point SMP3 or by DSC measurements (Mettler DSC 20) taking peak onsets. NMR spectra were obtained with Bruker DRX 400 (^{1}H: NMR 400.14 MHz; ^{13}C: NMR 100.62 MHz) or Bruker Avance 2 (^{1}H: NMR 600.13 MHz; ^{13}C: NMR 150.90 MHz) spectrometers; the samples were measured as $CDCl_3$ solutions. ^{1}H NMR chemical shifts (δ) are given in ppm relative to TMS as internal standard, ^{13}C shifts relative to $CDCl_3$ ($\delta = 77.3$ ppm). Data are reported as follows: s = singlet, d = doublet, dd = doublet of doublet, t = triplet. Free base porphyrins showed the α- and β-carbon signals of the pyrrole unit merging into one broad signal because of the tautomeric NH protons.[22] Appellation of the hydrogen and carbon atoms is defined in the Supporting Information. Mass spectra measurements (EI and ESI) were performed at the Institut für Organische Chemie, Technische Universität Braunschweig with a MAT 95 (Thermofinnigan) instrument; Low-resolution EI (electron ionisation at 70 eV), or high-resolution EI with peak matching method at a resolution of 10000 with PFK as mass calibrant. ESI mass spectra were obtained with a MAT 95XLT (Thermofinnigan) instrument. Concentrations were approx. 50 µL/mL, solvents are noted in the analytical section. Spray voltages in positive mode were 1.3–1.8 kV. APCI high-resolution mass spectra were recorded at the IOCB AS, Prague with a LTQ Orbitrap XL (Thermo Fisher Scientific) instrument, low-resolution spectra with a LC Fleet (Thermo Fisher Scientific) instrument. UV/Vis and IR spectra were recorded with Carry 100 Bio (Varian) and ATR Diamond Tensor 27 (Bruker) spectrometers. IR bands are characterised by intensity: w = weak, m = medium, s = strong. Elemental analyses were performed at the Institut für Pharmazeutische Chemie, Technische Universität Braunschweig. Cyclic voltammetry was performed with a Metrohm µAutolab instrument equipped with a 1-mm platin disc working electrode, a platin wire counter electrode and a saturated Ag/AgCl reference electrode. The electrolyte Bu_4NPF_6 was dissolved in anhydrous dichloromethane, which was stored under a nitrogen atmosphere, to generate a 0.1 M oxygen-free stock solution. Monomer concentrations were set to 0.1 mM. Scan rate was set to 100 mV/s. The ferrocene/ferrocenium redox couple was determined at 0.65 V. Compounds **1**,[7] **5**,[7] **9**,[7] **13**,[10] **14**,[11] **15**,[23] **17**,[24] **19**[11,12] and **20**[13] were synthesised according to literature procedures.

General Procedure for Metal Insertion. Method IA: The free base porphyrin and the metal acetate were heated in DMF. After the reaction was complete, water was added and the precipitate was filtered off and washed. The solid was either crystallised from CH_2Cl_2/MeOH or purified by flash column chromatography.

Method IB: The free base porphyrin and the metal acetate were heated in either DMF or a mixture of THF/$CHCl_3$/MeOH. After the reaction was complete the solution was cooled to r.t. and CH_2Cl_2 was added. Washing the organic phase and drying over $MgSO_4$ gave the product after crystallisation from CH_2Cl_2/MeOH or flash column chromatography.

General Procedure for Horner–Emmons Reaction. Method II: The aldehyde and the phosphonate **15** were dissolved in DME. NaH (60% in mineral oil) was added at r.t. and the mixture was stirred. After reaction (completion was indicated by TLC), water was added and the mixture was extracted with CH_2Cl_2. The combined organic phases were dried with $MgSO_4$, the solvents removed and the crude product was purified by flash column chromatography.

General Procedure for Suzuki Coupling. Method III: A solution of the corresponding 2,5-bromothiophene, $Pd(PPh_3)_4$, boronic acid **17**, aqueous Na_2CO_3 solution and either DME or DMF was heated to reflux and rigorously stirred. After the reaction was complete (indicated by TLC), the reaction mixture was cooled to room temp. and water was added. The mixture was extracted and the combined organic phases were dried with $MgSO_4$. Removing the solvents and purification of the crude product by crystallisation or flash column chromatography gave the desired product.

{5,15-Bis[4-(hexoxy)thien-2-yl]-10,20-diphenylporphyrinato}-copper(II) (2): (Method IB) Compound **1** (200 mg, 242 µmol), $Cu(OAc)_2\cdot H_2O$ (242 mg, 1.21 mmol), MeOH (5 mL), THF (10 mL), $CHCl_3$ (10 mL), 1 h reflux, adding CH_2Cl_2 (30 mL), washing with aqueous saturated NH_4Cl (30 mL) and H_2O (2 × 30 mL), and recrystallisation from CH_2Cl_2/MeOH (30 mL/5 mL) gave **2** (190 mg, 214 µmol, 88%); purple crystals; m.p. 207 °C (DSC peak onset). MS (EI): *m*/*z* (%) = 887/888/889/890/891/892 (100/58/69/33/13) $[M]^{+\cdot}$. HRMS (EI): calcd. for $C_{52}H_{48}CuN_4O_2S_2$ $[M]^{+\cdot}$ 887.2515; found 887.2480. FTIR: $\tilde{\nu}$ = 3110 (w), 3049 (w), 2923 (w), 2856 (w), 1555 (w), 1512 (w), 1458 (m), 1440 (w), 1359 (m), 1208 (w), 1166 (s), 1072 (m), 1048 (w), 1029 (w), 1001 (s), 969 (m), 872 (w), 812 (m), 792 (s), 754 (m), 700 (m) cm^{-1}. UV/Vis: λ (ε) = 575 (6200), 541 (21200), 418 (381600) nm. $C_{52}H_{48}CuN_4O_2S_2$ (888.64): calcd. C 70.28, H 5.44, N 6.30, S 7.22; found C 70.02, H 5.48, N 6.55, S 6.68.

{5,15-Bis[4-(hexoxy)thien-2-yl]-10,20-diphenylporphyrinato}zinc(II) (3): (Method IA) Compound **1** (400 mg, 484 µmol), $Zn(OAc)_2$ (1000 mg, 6.44 mmol), DMF (20 mL), 1 h at 80 °C, adding H_2O (100 mL), and two times recrystallisation from CH_2Cl_2/MeOH (40 mL/10 mL) gave **3** (400 mg, 449 µmol, 93%); purple crystals; m.p. 184 °C (DSC peak onset). ^{1}H NMR (600 MHz): δ = 9.23 (d, $^3J_{8,7}$ = 4.6 Hz, 4 H, 8-H), 8.93 (d, $^3J_{7,8}$ = 4.6 Hz, 4 H, 7-H), 8.22–8.18 (m, 4 H, 3-H), 7.79–7.72 (m, 6 H, 1,2-H), 7.60 (d, $^4J_{12,14}$ = 1.8 Hz, 2 H, 12-H), 6.70 (d, $^4J_{14,12}$ = 1.8 Hz, 2 H, 14-H), 4.18 (t, $^3J_{15,16}$ = 6.7 Hz, 4 H, 15-H), 1.93–1.87 (m, 4 H, 16-H), 1.59–1.53 (m, 4 H, 17-H), 1.45–1.36 (m, 8 H, 18,19-H), 0.94 (t, $^3J_{20,19}$ = 7.1 Hz, 6 H, 20-H) ppm. ^{13}C NMR (150 MHz): δ = 156.0 (s, C-13), 150.7 (s, C-9), 150.5 (s, C-6), 142.6 (s, C-4), 142.5 (s, C-11), 134.4 (d, C-3), 132.2 (d, C-7), 131.9 (d, C-8), 127.6 (d, C-1), 126.6 (d, C-2), 126.3 (d, C-12), 121.8 (s, C-5), 112.8 (s, C-10), 99.8 (d, C-14), 70.3 (t, C-15), 31.7 (t, C-18), 29.4 (t, C-16), 25.9 (t, C-17), 22.7 (t, C-19), 14.1 (q, C-20) ppm. MS (EI): *m*/*z* (%) = 888/889/890/891/892/893 (100/54/75/48/54/26/10) $[M]^{+\cdot}$. HRMS (EI): calcd. for $C_{52}H_{48}N_4O_2S_2Zn$ $[M]^{+\cdot}$ 888.2510; found 888.2497. FTIR: $\tilde{\nu}$ = 3109 (w), 2925 (w), 2853 (w), 1552 (w), 1496 (w), 1456 (w), 1362 (m), 1336 (m), 1208 (w), 1164 (m), 1070 (w), 1022 (m), 989 (m), 969 (m), 871 (w), 823 (w), 809 (w), 793 (s), 744 (m), 717 (m), 702 (s) cm^{-1}. UV/Vis: λ (ε) = 592 (5600), 550 (19600), 422 (400000) nm. $C_{52}H_{48}N_4O_2S_2Zn$ (890.50): calcd. C 70.14, H 5.43, N 6.29, S 7.20; found C 69.33, H 5.52, N 6.27, S 6.89.

{5,15-Bis[4-(hexoxy)thien-2-yl]-10,20-diphenylporphyrinato}-cobalt(II) (4): (Method IB) Compound **1** (200 mg, 242 µmol), $Co(OAc)_2{\cdot}4H_2O$ (850 mg, 3.41 mmol), DMF (15 mL), 1 h reflux, adding CH_2Cl_2 (50 mL), washing with H_2O (5 × 50 mL), and two times recrystallisation from CH_2Cl_2/MeOH (20 mL/5 mL) gave **4** (170 mg, 192 µmol, 79%); red-brownish solid; m.p. 177 °C (DSC peak onset). MS (EI): *m*/*z* (%) = 883/884/885 (100/53/27) $[M]^{+\cdot}$. HRMS (EI): calcd. for $C_{52}H_{48}CoN_4O_2S_2$ $[M]^{+\cdot}$ 883.2551; found 883.2533. FTIR: $\tilde{\nu}$ = 2952 (w), 2927 (w), 2856 (w), 1557 (w), 1536 (w), 1462 (w), 1442 (w), 1363 (m), 1167 (s), 1068 (m), 1003 (m), 974 (m), 814 (m), 791 (s), 747 (m), 715 (m) cm^{-1}. UV/Vis: λ (ε) = 559 (sh.), 533 (15000), 414 (195700) nm. $C_{52}H_{48}CoN_4O_2S_2$ (884.03): calcd. C 70.65, H 5.47, N 6.34, S 7.25; found C 70.44, H 5.48, N 6.52, S 6.98.

{5,15-Bis[3,4′-bis(hexoxy)-2,2′-bithiophen-5-yl]-10,20-diphenylporphyrinato}copper(II) (6): (Method IB) Compound **5** (210 mg, 176 µmol), $Cu(OAc)_2{\cdot}H_2O$ (170 mg, 851 µmol), MeOH (5 mL), THF (10 mL), $CHCl_3$ (10 mL), 1 h reflux, washing with H_2O (2 × 50 mL), and recrystallisation from CH_2Cl_2/MeOH (30 mL/10 mL) gave **6** (200 mg, 160 µmol, 90%); purple crystals; m.p. 170 °C (DSC peak onset). MS (ESI MeOH): (%) *m*/*z* = 1251/1252/1253/1254/1255/1256 (75/92/100/76/47/15) $[M^{+\cdot}/M + H^+]$. MS (APCI, $CHCl_3$): *m*/*z* (%) = 1252/1253/1254/1255/1256/1257 (39/100/84/59/24/22) $[M + H^+]$. HRMS (APCI, $CHCl_3$): calcd. for $C_{72}H_{77}CuN_4O_4S_4$ $[M + H^+]$ 1252.4118; found 1252.4095. FTIR: $\tilde{\nu}$ = 3108 (w), 3056 (w), 3025 (w), 2925 (m), 2857 (m), 1544 (m), 1520 (w), 1463 (w), 1347 (s), 1311 (w), 1206 (w), 1168 (s), 1123 (w), 1072 (m), 997 (s), 976 (m), 926 (w), 904 (w), 864 (w), 816 (m), 796 (s), 749 (m), 717 (m) cm^{-1}. UV/V: λ (ε) = 591 (10500), 546 (21600), 417 (202000) nm. $C_{72}H_{76}CuN_4O_4S_4$ (1253.2): calcd. C 69.00, H 6.11, N 4.47, S 10.23; found C 68.60, H 5.99, N 4.58, S 10.02.

{5,15-Bis[3,4′-bis(hexoxy)-2,2′-bithiophen-5-yl]-10,20-diphenyl-porphyrinato}zinc(II) (7): (Method IA) Compound **5** (230 mg, 242 µmol), $Zn(OAc)_2$ (370 mg, 2.02 mmol), DMF (10 mL), 1 h at 140 °C, addition of H_2O (50 mL), washing with H_2O and MeOH, and flash chromatography (hexane/CH_2Cl_2, 1:1, R_f = 0.46) gave **7** (310 mg, 104 µmol, 53%); purple solid; m.p. > 230 °C (decomp.). ^1H NMR (600 MHz): δ = 9.31 (d, ^3J = 4.6 Hz, 4 H, 8-H), 8.96 (d, ^3J = 4.6 Hz, 4 H, 7-H), 8.23–8.18 (m, 4 H, 3-H), 7.81–7.73 (m, 6 H, 1,2-H), 7.67 (s, 2 H, 12-H), 7.01 (d, ^4J = 1.5 Hz, 2 H, 22-H), 6.14 (d, ^4J = 1.5 Hz, 2 H, 24-H), 4.31 (d, ^3J = 6.5 Hz, 4 H, 25-H), 3.91 (d, ^3J = 6.5 Hz, 4 H, 25-H), 1.99–1.93 (m, 4 H, 16-H), 1.77–1.71 (m, 4 H, 26-H), 1.64–1.57 (m, 4 H, 17-H), 1.46–1.29 (m, 20 H, 18,19,27,28,29-H), 0.96–0.87 (m, 12 H, 20,30-H) ppm. ^{13}C NMR (150 MHz): δ = 157.1 (s, C-23), 151.6 (s, C-13), 150.7 (s, C-9), 150.5 (s, C-6), 142.5 (s, C-4), 139.1 (s, C-11), 134.4 (d, C-3), 133.6 (s, C-21), 132.5 (d, C-7), 131.8 (d, C-8), 127.7 (d, C-1), 126.6 (d, C-2), 124.3 (d, C-12), 122.0 (s, C-5), 118.3 (s, C-14), 114.5 (d, C-22), 112.4 (s, C-10), 95.8 (d, C-24), 72.2 (t, C-15), 70.1 (t, C-25), 31.60 (t, C-18,28), 29.7 (t, C-16), 29.2 (t, C-26), 25.8 (t, C-17), 25.7 (t, C-27), 22.63 (t, C-19), 22.62 (t, C-29), 14.09 (q, C-20), 14.08 (q, C-30) ppm. MS (ESI MeOH): *m*/*z* (%) = 1252/1253/1254/1255/1256/1257/1258/1259 (57/96/100/91/97/ 68/42/17) $[M^{+\cdot}/M + H^+]$. MS (APCI, $CHCl_3$): *m*/*z* (%) = 1253/1254/1255/1256/1257/1258/1259 (67/100/77/61/ 75/36/22) $[M + H^+]$. HRMS (APCI, $CHCl_3$): calcd. for $C_{72}H_{77}ZnN_4O_4S_4$ $[M + H^+]$ 1253.4114; found 1253.4093. FTIR: $\tilde{\nu}$ = 3109 (w), 3054 (w), 2950 (m), 2924 (m), 2854 (m), 1569 (m), 1540 (m), 1497 (w), 1462 (w), 1439 (w), 1397 (w), 1356 (m), 1206 (w), 1167 (m), 1069 (m), 993 (s), 974 (m), 863 (w), 791 (s), 751 (w), 717 (m) cm^{-1}. UV/Vis: λ (ε) = 603 (13200), 554 (20400), 423 (212900) nm. $C_{72}H_{76}N_4O_4S_4Zn$ (1255.07): calcd. C 68.90, H 6.10, N 4.46, S 10.22; found C 68.98, H 6.18, N 4.45, S 9.79.

{5,15-Bis[3,4′-bis(hexoxy)-2,2′-bithiophen-5-yl]-10,20-diphenylporphyrinato}cobalt(II) (8): (Method IB) Compound **5** (250 mg, 210 µmol), $Co(OAc)_2{\cdot}4H_2O$ (600 mg, 2.41 mmol), DMF (15 mL), 1 h 140 °C, addition of CH_2Cl_2 (100 mL), washing with saturated aqueous NH_4Cl (3 × 50 mL), H_2O (50 mL) and brine (50 mL), and removal of solvents gave **8** (200 mg, 160 µmol, 76%); purple solid; m.p. 104 °C (DSC peak onset). MS (ESI MeOH): *m*/*z* (%) = 1247/1248/1249/1250 (100/86/54/27) $[M^{+\cdot}/M + H^+]$. MS (APCI, $CHCl_3$): *m*/*z* (%) = 1247/1248/1249/1250 (57/100/59/49) $[M^{+\cdot}/M + H^+]$. HRMS (APCI, $CHCl_3$): calcd. for $C_{72}H_{77}CoN_4O_4S_4$ $[M + H^+]$ 1248.4154; found 1248.4126. FTIR: $\tilde{\nu}$ = 3119 (w), 3056 (w), 2925 (m), 2855 (m), 1566 (m), 1541 (m), 1459 (m), 1399 (w), 1353 (s), 1167 (m), 1073 (m), 1002 (s), 985 (m), 863 (w), 792 (s), 751 (m) cm^{-1}. UV/Vis: λ (ε) = 575 (sh.), 535 (17200), 415 (135900) nm. $C_{72}H_{76}CoN_4O_4S_4$ (1248.59): calcd. C 69.26, H 6.14, N 4.49, S 10.27; found C 69.17, H 6.13, N 4.61, S 9.70.

{5,15-Bis[3,3′,4′′-tris(hexoxy)-2,5′:2′,2′′-terthiophen-5-yl]-10,20-diphenylporphyrinato}copper(II) (10): (Method IB) Compound **9** (160 mg, 105 µmol), $Cu(OAc)_2{\cdot}H_2O$ (130 mg, 650 µmol), MeOH (2.5 mL), THF (5 mL), $CHCl_3$ (5 mL), 1 h reflux, cooling to r.t. and removing the solvents gave the crude product that was purified by flash chromatography (hexane/CH_2Cl_2, 3:2, R_f = 0.46) to give **10** (100 mg, 62 µmol, 60%); purple solid; m.p. > 250 °C (decomp.). MS (ESI ACN/Toluene): *m*/*z* (%) = 1616/1617/1618/1619/1620/1621/1622/1623 (7/76/85/100/77/81/29/17) $[M^{+\cdot}/M + H^+]$. MS (APCI, $CHCl_3$): *m*/*z* (%) = 1617/1618/1619/1620/1621/1622 (86/100/98/74/48/24) $[M + H^+]$. HRMS (APCI, $CHCl_3$): calcd. for $C_{92}H_{105}CuN_4O_6S_6$ $[M + H^+]$ 1616.5654; found 1616.5633. FTIR: $\tilde{\nu}$ = 3110 (w), 3056 (w), 2925 (m), 2855 (m), 1569 (m), 1536 (m), 1455 (m), 1403 (w), 1349 (s), 1168 (m), 1071 (s), 1001 (s), 977 (m), 793 (s), 752 (m), 716 (m) cm^{-1}. UV/Vis: λ (ε) = 598 (17400), 547 (25900), 418 (226300) nm. $C_{92}H_{104}CuN_4O_6S_6$ (1617.77): calcd. C 68.30, H 6.48, N 3.46, S 11.89; found C 68.66, H 6.60, N 3.62, S 11.46.

{5,15-Bis[3,3′,4′′-tris(hexoxy)-2,5′:2′,2′′-terthiophen-5-yl]-10,20-diphenylporphyrinato}zinc(II) (11): (Method IA) Compound **9** (290 mg, 186 µmol), $Zn(OAc)_2$ (370 mg, 2.02 mmol), DMF (10 mL), 1 h at 80 °C, adding H_2O (50 mL), and two times flash chromatography (hexane/CH_2Cl_2, 1:1, R_f = 0.54) gave **11** (160 mg, 99 µmol, 53%); purple solid; m.p. 92 °C (DSC peak onset). ^1H NMR (600 MHz): δ = 9.32 (d, $^3J_{8,7}$ = 4.6 Hz, 4 H, 8-H), 8.96 (d, $^3J_{7,8}$ = 4.6 Hz, 4 H, 7-H), 8.23–8.19 (m, 4 H, 3-H), 7.79–7.72 (m, 6 H, 1,2-H), 7.64 (s, 2 H, 12-H), 6.90 (s, 2 H, 22-H), 6.73 (d, $^4J_{32,34}$ = 1.7 Hz, 2 H, 32-H), 5.99 (d, $^4J_{34,32}$ = 1.7 Hz, 2 H, 34-H), 4.29 (t, $^3J_{15,16}$ = 6.4 Hz, 4 H, 15-H), 3.88 (t, $^3J_{25,26}$ = 6.6 Hz, 4 H, 25-H), 3.85 (t, $^3J_{35,36}$ = 6.6 Hz, 4 H, 35-H), 1.98–1.90 (m, 4 H, 16-H), 1.75–1.59 (m, 12 H, 36,26,17-H), 1.46–1.26 (m, 32 H, 27,37,18,28,38,19,29,39-H), 0.94 (t, ^3J = 7.1 Hz, 6 H, 20/30/40-H), 0.91 (t, ^3J = 7.1 Hz, 6 H, 20/30/40-H), 0.88 (t, ^3J = 7.0 Hz, 6 H, 20/30/40-H) ppm. ^{13}C NMR (150 MHz): δ = 157.0 (s, C-33), 152.3 (s, C-23), 151.9 (s, C-13), 150.7 (s, C-9), 150.6 (s, C-6), 142.5 (s, C-4), 139.3 (s, C-11), 134.5 (d, C-3), 133.9 (s, C-31), 132.5 (d, C-7), 131.8 (d, C-8), 130.5 (s, C-21), 127.6 (d, C-1), 126.6 (d, C-2), 124.3 (d, C-12), 122.1 (s, C-5), 118.4 (s, C-14), 113.74 (d, C-32), 113.70 (s, C-24), 112.3 (s, C-10), 112.0 (d, C-22), 95.2 (d, C-34), 72.3 (t, C-15), 71.7 (t, C-25), 70.0 (t, C-35), 31.64 (t, C-18/28/38), 31.61 (t, C-18/28/38), 31.5 (t, C-18/28/38), 29.7 (t, C-16), 29.4 (t, C-26), 29.2 (t, C-36), 25.9 (t, C-17/27/37), 25.7 (t, C-17/27/37), 25.6 (t, C-17/27/37), 22.7 (t, C-19/29/39), 22.63 (t, C-19/29/39), 22.57 (t, C-19/29/39), 14.12 (q, C-20/30/40), 14.08 (q, C-20/30/40), 14.04 (q, C-20/30/40) ppm. MS (ESI ACN/Toluene): *m*/*z* (%) = 1617/1618/1619/1620/1621/1622/1623/1624/1625 (39/79/95/100/94/84/63/43/28) $[M^{+\cdot}/M + H^+]$. MS (APCI, $CHCl_3$): *m*/*z* (%) = 1618/1619/1620/1621/1622/

1623/1624/1625 (68/80/100/78/88/56/42/20) [M + H$^+$]. HRMS (APCI, CHCl$_3$): calcd. for $C_{92}H_{105}N_4O_6S_6Zn$ [M + H$^+$] 1617.5650; found 1617.5624. FTIR: $\tilde{\nu}$ = 3112 (w), 3055 (w), 2924 (m), 2854 (m), 1569 (m), 1535 (m), 1457 (m), 1439 (w), 1401 (w), 1352 (s), 1207 (m), 1168 (m), 1070 (s), 997 (m), 974 (m), 907 (w), 792 (s), 752 (w), 718 (m) cm^{-1}. UV/Vis: λ (ε) = 613 (21200), 555 (23600), 425 (228400) nm. $C_{92}H_{104}N_4O_6S_6Zn$ (1619.63): calcd. C 68.22, H 6.47, N 3.46, S 11.88; found C 67.96, H 6.45, N 3.66, S 11.73.

{5,15-Bis[3,3′,4′′-tris(hexoxy)-2,5′:2′,2′′-terthiophen-5-yl]-10,20-diphenylporphyrinato}cobalt(II) (12): (Method IA) Compound **9** (150 mg, 96 µmol), Co(OAc)$_2$·4H$_2$O (400 mg, 1.61 mmol), DMF (7.5 mL), 1 h, 80 °C, adding H$_2$O (50 mL), washing with H$_2$O and MeOH. The solid was recrystalised from MeOH/CH$_2$Cl$_2$ (5 mL/15 mL) and the methanol phase was cooled to –18 °C for some days. The precipitated solid was filtered off to give **12** (86 mg, 53 µmol, 56%); purple solid; m.p. > 240 °C (decomp.). MS (ESI ACN/Toluene): *m/z* (%) = 1612/1613/1614/1615/1616/1617 (78/100/87/57/32/16) [M$^{+\cdot}$/M + H$^+$]. MS (APCI, CHCl$_3$): *m/z* (%) = 1613/1614/1615/1616/1617 (100/98/76/40/22) [M + H$^+$]. HRMS (APCI, CHCl$_3$): calcd. for $C_{92}H_{105}CoN_4O_6S_6$ [M + H$^+$] 1612.5690; found 1612.5671. FTIR: $\tilde{\nu}$ = 3112 (w), 3056 (w), 2926 (m), 2856 (m), 1569 (m), 1536 (m), 1455 (m), 1403 (w), 1353 (s), 1169 (m), 1073 (s), 1003 (m), 984 (m), 905 (w), 793 (s), 751 (m), 715 (m) cm^{-1}. UV/Vis: λ (ε) = 585 (10900), 537 (19000), 417 (157800) nm. $C_{92}H_{104}CoN_4O_6S_6$ (1613.16): calcd. C 68.50, H 6.50, N 3.47, S 11.39; found C 68.16, H 6.24, N 3.40, S 11.62.

{10-[2-(2,5-Dibromothien-3-yl)vinyl]-5,15-diphenylporphyrinato}copper(II) (16): (Method II) Compound **14** (300 mg, 543 µmol), **15** (240 mg, 633 µmol), DME (9 mL), NaH (60% in mineral oil, 82 mg, 2.05 mmol), 22 h at r.t., adding H$_2$O (25 mL), extraction with CH$_2$Cl$_2$ (3 × 30 mL), and purification by flash chromatography (hexane/CH$_2$Cl$_2$, 1:1, R_f = 0.72) gave **16** (320 mg, 405 µmol, 74%); purple solid; m.p. 287 °C. MS (EI): *m/z* = 787/788/789/790/791/792/793 (35/15/100/38/81/31/24) [M$^{+\cdot}$], 707/708/709/710/711/712/713 (12/36/51/64/66/38/24) [M$^{+\cdot}$ – Br], 627/628/629/620/621/622/ 623 (8/20/15/32/16/33) [M$^{+\cdot}$ – 2×Br]. MS (APCI, CHCl$_3$): *m/z* (%) = 788/789/790/791/792/793/794 (48/34/100/50/94/42/28) [M + H$^+$]. HRMS (APCI, CHCl$_3$): calcd. for $C_{38}H_{23}Br_2CuN_4S$ [M + H$^+$] 787.9277; found 787.9306. FTIR: $\tilde{\nu}$ = 3098 (w), 3053 (w), 3027 (w), 2922 (w), 2852 (w), 1598 (w), 1527 (w), 1489 (w), 1441 (w), 1381 (w), 1327 (w), 1208 (w), 1156 (w), 1065 (w), 995 (m), 965 (m), 951 (m), 928 (w), 906 (w), 857 (m), 823 (m), 783 (s), 745 (m), 725 (m) cm^{-1}. UV/Vis: λ (ε) = 582 (6200), 541 (16100), 419 (247500) nm. $C_{38}H_{22}Br_2CuN_4S$ (790.03): calcd. C 57.77, H 2.81, N 7.09, S 4.06; found C 58.59, H 2.90, N 7.34, S 4.02.

{10-{2-[3,4′′-Bis(hexoxy)-2,2′:5′,2′′-terthiophen-3′-yl]vinyl}-5,15-diphenylporphyrinato}copper(II) (18): (Method III) Compound **16** (383 mg, 485 µmol), **17** (332 mg, 1.45 mmol), Pd(PPh$_3$)$_4$ (70 mg, 61 µmol, 6 mol-%), DME (30 mL), 1 M aqueous Na$_2$CO$_3$ (15 mL), 3 h reflux, adding H$_2$O (50 mL), extraction with CH$_2$Cl$_2$ (3 × 70 mL), purification by flash chromatography (hexane/CH$_2$Cl$_2$, 2:1, R_f = 0.54), and recrystallisation from MeOH/CH$_2$Cl$_2$ (40 mL/10 mL) gave **18** (400 mg, 401 µmol, 82%); purple solid; m.p. 152 °C. MS (EI): *m/z* (%) = 995/996/997/998/999 (100/64/74/39/19) [M]$^{+\cdot}$. MS (APCI, CHCl$_3$): *m/z* (%) = 996/997/998/999/1000 (100/74/98/46/26) [M + H$^+$]. HRMS (APCI, CHCl$_3$): calcd. for $C_{58}H_{53}CuN_4O_2S_3$ [M + H$^+$] 996.2590; found 996.2621. FTIR: $\tilde{\nu}$ = 3114 (w), 3050 (w), 2925 (w), 2855 (w), 1596 (w), 1553 (w), 1526 (m), 1489 (w), 1440 (w), 1350 (m), 1208 (w), 1165 (m), 1064 (m), 995 (m), 967 (w), 954 (w), 921 (w), 841 (w), 814 (m), 786 (s), 750 (m), 719 (m) cm^{-1}. UV/Vis: λ (ε) = 586 (8200), 542 (15900), 417 (174400) nm. $C_{58}H_{52}CuN_4O_2S_3$ (996.80): calcd. C 69.89, H 5.26, N 5.62, S 9.65; found C 68.07, H 5.12, N 5.49, S 9.30.

{10-[2-(2,5-Dibromothien-3-yl)vinyl]-5,15-diphenylporphyrinato}zinc(II) (21): (Method II) Compound **20** (260 mg, 470 µmol), **15** (202 mg, 534 µmol), DME (7 mL), NaH (60% in mineral oil, 73 mg, 1.75 mmol), 4 h at r.t., adding H$_2$O (20 mL), extraction with CH$_2$Cl$_2$ (3 × 60 mL), washing with brine (50 mL), and purification by flash chromatography (CH$_2$Cl$_2$; R_f = 0.95) gave **21** (275 mg, 347 µmol, 70%); purple solid; m.p. >290 °C. ^{1}H NMR (600 MHz): δ = 10.07 (s, 1 H, 15-H), 9.45 (d, $^3J_{8,7}$ = 4.6 Hz, 2 H, 8-H), 9.42 (d, $^3J_{16,17}$ = 16.0 Hz, 1 H, 16-H), 9.27 (d, $^3J_{13,12}$ = 4.4 Hz, 2 H, 13-H), 9.00 (d, $^3J_{12,13}$ = 4.4 Hz, 2 H, 12-H), 8.98 (d, $^3J_{7,8}$ = 4.6 Hz, 2 H, 7-H), 8.21–8.18 (m, 4 H, 3-H), 7.83–7.76 (m, 6 H, 1,2-H), 7.81 (s, 1 H, 20-H), 7.22 (d, $^3J_{17,16}$ = 16.0 Hz, 1 H, 17-H) ppm. ^{13}C NMR (150 MHz): δ = 150.0 (s, C-11), 149.8 (s, C-14), 149.7 (s, C-6), 148.6 (s, C-9), 142.5 (s, C-4), 140.0 (s, C-19), 134.5 (d, C-3), 133.3 (d, C-17), 132.6 (d, C-12), 132.4 (d, C-16), 132.1 (d, C-7), 131.7 (d, C-13), 129.7 (d, C-8), 127.7 (d, C-20), 127.5 (d, C-1), 126.6 (d, C-2), 120.8 (s, C-5), 116.7 (s, C-10), 112.3 (s, C-21), 111.2 (s, C-18), 106.0 (s, C-15) ppm. MS (ESI MeOH/CHCl$_3$): *m/z* (%) = 788/789/790/791/792/793/794/795/796 (38/17/93/47/100/52/62/26/25) [M$^{+\cdot}$/M + H$^+$]. MS (APCI, MeOH/CHCl$_3$): *m/z* = 788/789/790/791/792/793/794/795/796 (38/24/81/48/ 100/57/60/35/20) [M$^{+\cdot}$/M+H$^+$]. HRMS (APCI, MeOH/CHCl$_3$): calcd. for $C_{38}H_{22}Br_2N_4SZn$ [M$^{+\cdot}$] 787.9218; found 787.9223. FTIR: $\tilde{\nu}$ = 3044 (w), 1593 (w), 1519 (w), 1486 (w), 1437 (w), 1420 (w), 1383 (w), 1318 (w), 1209 (w), 1154 (w), 1065 (m), 996 (s), 970 (m), 952 (m), 929 (w), 853 (m), 824 (w), 785 (s), 754 (m), 724 (m), 702 (s) cm^{-1}. UV/Vis: λ (ε) = 594 (7900), 551 (16100), 424 (274600) nm. $C_{38}H_{22}Br_2N_4SZn$ (791.89): calcd. C 57.64, H 2.80, N 7.08, S 4.05; found C 58.06, H 3.17, N 7.05, S 4.13.

(10-{2-[3,4′′-Bis(hexoxy)-2,2′:5′,2′′-terthiophen-3′-yl]vinyl}-5,15-diphenylporphyrinato)zinc(II) (22): (Method III) Compound **21** (160 mg, 202 µmol), **17** (140 mg, 613 µmol), Pd(PPh$_3$)$_4$ (40 mg, 35 µmol, 9 mol-%), DME (15 mL), 1 M aqueous Na$_2$CO$_3$ (8 mL), 5 h reflux, adding H$_2$O (30 mL), extraction with CH$_2$Cl$_2$ (3 × 30 mL), and purification by flash chromatography (hexane/CH$_2$Cl$_2$, 1:1; R_f = 0.90) gave **22** (130 mg, 130 µmol, 64%); dark solid; m.p. 178 °C. ^{1}H NMR (600 MHz): δ = 9.89 (s, 1 H, 15-H), 9.38 (d, $^3J_{8,7}$ = 4.6 Hz, 2 H, 8-H), 9.31 (d, $^3J_{16,17}$ = 15.8 Hz, 2 H, 16-H), 9.16 (d, $^3J_{13,12}$ = 4.4 Hz, 2 H, 13-H), 8.93 (d, $^3J_{12,13}$ = 4.4 Hz, 2 H, 12-H), 8.88 (d, $^3J_{7,8}$ = 4.6 Hz, 2 H, 7-H), 8.18–8.14 (m, 4 H, 3-H), 7.86 (s, 1 H, 24-H), 7.81–7.73 (m, 6 H, 1,2-H), 7.43 (d, $^3J_{17,16}$ = 15.8 Hz, 2 H, 17-H), 6.91 (d, $^4J_{27,29}$ = 1.7 Hz, 1 H, 27-H), 6.82 (d, $^4J_{20,18}$ = 1.7 Hz, 1 H, 20-H), 6.09 (d, $^4J_{29,27}$ = 1.7 Hz, 1 H, 29-H), 6.06 (d, $^4J_{18,20}$ = 1.7 Hz, 1 H, 18-H), 3.91 (d, $^3J_{36,37}$ = 6.5 Hz, 2 H, 36-H), 3.72 (d, $^3J_{30,31}$ = 6.5 Hz, 2 H, 30-H), 1.81–1.75 (m, 2 H, 37-H), 1.58–1.51 (m, 2 H, 31-H), 1.51–1.44 (m, 2 H, 38-H), 1.40–1.34 (m, 4 H, 39,40-H), 1.27–1.20 (m, 2 H, 32-H), 1.19–1.11 (m, 4 H, 33,34-H), 0.96–0.91 (m, 3 H, 41-H), 0.77–0.72 (m, 3 H, 35-H) ppm. ^{13}C NMR (150 MHz): δ = 157.6 (s, C-28), 157.5 (s, C-19), 149.8 (s, C-11), 149.58 (s, C-14), 149.56 (s, C-6), 148.6 (s, C-9), 142.6 (s, C-4), 137.1 (s, C-23), 136.3 (s, C-25), 134.9 (s, C-26), 134.8 (d, C-17), 134.6 (d, C-3), 133.5 (s, C-21), 132.9 (s, C-22), 132.4 (d, C-12), 131.9 (d, C-7), 131.7 (d, C-16), 131.5 (d, C-13), 129.9 (d, C-8), 127.4 (d, C-1), 126.6 (d, C-2), 122.2 (d, C-24), 120.6 (s, C-5), 119.1 (d, C-20), 117.5 (s, C-10), 116.5 (d, C-27), 105.5 (d, C-15), 98.4 (d, C-18), 96.6 (d, C-29), 70.1 (t, C-36), 69.9 (t, C-30), 31.6 (t, C-39), 31.4 (t, C-33), 29.2 (t, C-37), 30.0 (t, C-31), 25.7 (t, C-38), 25.5 (t, C-32), 22.6 (t, C-34), 22.4 (t, C-40), 14.1 (q, C-41), 13.9 (q, C-35) ppm. MS (ESI MeOH): *m/z* (%) = 996/997/998/999/1000/1001/1002 (100/68/92/60/70/38/20) [M$^{+\cdot}$/M + H$^+$]. MS (APCI, MeOH/CHCl$_3$): *m/z* (%) = 996/997/998/999/1000/1001/1002 (94/90/100/73/70/ 56/24) [M$^{+\cdot}$/M + H$^+$]. HRMS (APCI, MeOH/CHCl$_3$): calcd. for $C_{58}H_{52}N_4O_2S_3Zn$ [M$^{+\cdot}$] 996.2538; found 996.2534. FTIR:

$\tilde{\nu}$ = 3112 (w), 3050 (w), 2925 (w), 2854 (w), 1553 (m), 1524 (w), 1486 (w), 1454 (w), 1439 (w), 1352 (m), 1210 (w), 1165 (m), 1062 (m), 995 (s), 967 (w), 953 (m), 921 (w), 843 (w), 814 (m), 782 (s), 750 (m) 720 (m) cm^{-1}. UV/Vis: λ (ε) = 598 (10900), 552 (16600), 423 (201600) nm. $C_{58}H_{52}N_4O_2S_3Zn$ (998.66): calcd. C 69.76, H 5.25, N 5.61, S 9.63; found C 69.88, H 5.22, N 5.85, S 9.33.

10-[2-(2,5-Dibromothien-3-yl)vinyl]-5,15-diphenylporphyrin (23): (Method II) Compound **19** (400 mg, 815 µmol), **15** (600 mg, 1.53 mmol), DME (10 mL), NaH (60% in mineral oil, 215 mg, 5.36 mmol), 6.5 h reflux, adding H_2O (30 mL), extraction with CH_2Cl_2 (5 × 50 mL), washing with brine (50 mL), and purification by flash chromatography (hexane/CH_2Cl_2, 1:2; R_f = 0.81) gave **23** (360 mg, 494 µmol, 60%); purple solid; m.p. >350 °C. ^1H NMR (600 MHz): δ = 10.14 (s, 1 H, 15-H), 9.52 (d, $^3J_{16,17}$ = 16.0 Hz, 1 H, 16-H), 9.49 (d, $^3J_{8,7}$ = 4.7 Hz, 2 H, 8-H), 9.28 (d, $^3J_{13,12}$ = 4.5 Hz, 2 H, 12,13-H), 8.96 (d, $^3J_{12,13}$ = 4.4 Hz, 2 H, 12-H), 8.95 (d, $^3J_{7,8}$ = 4.7 Hz, 2 H, 7-H), 8.25–8.21 (m, 4 H, 3-H), 7.83–7.77 (m, 6 H, 20-H), 7.80 (s, 1 H, 1,2-H), 7.27 (d, $^3J_{17,16}$ = 16.0 Hz, 1 H, 17-H), –2.85 (s, 2 H, tautomeric NH) ppm. ^{13}C NMR (150 MHz): δ = 146.5 (br. signal, α-pyrrol-C-6,9,11,14), 141.7 (s, C-4), 139.9 (s, C-19), 134.6 (d, C-3), 134.1 (d, C-17), 132.0 (d, C-16), 131.2 (br. signal, β-pyrrol-C-7,12,13), 129.3 (br. signal, β-pyrrol-C-8), 127.8 (d, C-1), 127.7 (d, C-20), 126.8 (d, C-2), 120.0 (s, C-5), 116.1 (s, C-10), 112.4 (s, C-21), 111.6 (s, C-18), 105.1 (d, C-15) ppm. MS (EI): m/z (%) = 726/727/728/729/730/731 (46/26/100/39/59/18) $[M]^{+\cdot}$. HRMS (EI): calcd. for $C_{38}H_{24}Br_2N_4S$ $[M]^{+\cdot}$ 726.0088; found 726.0063. FTIR: $\tilde{\nu}$ = 3304 (w), 3092 (w), 3053 (w), 3026 (w), 1596 (w), 1554 (w), 1477 (w), 1440 (w), 1403 (w), 1340 (w), 1240 (w), 1195 (w), 1152 (w), 1067 (w), 1048 (w), 1003 (w), 969 (m), 957 (m), 929 (m), 853 (m), 823 (w), 785 (s), 730 (s) cm^{-1}. UV/Vis: λ (ε) = 652 (4300), 591 (sh.), 557 (11500), 517 (13900) 422 (272500) nm. $C_{38}H_{24}Br_2N_4S$ (728.50): calcd. C 62.65, H 3.32, N 7.69, S 4.40; found C 62.15, H 3.43, N 7.97, S 4.43.

10-{2-[3,4′′-Bis(hexoxy)-2,2′:5′,2′′-terthiophen-3′-yl]vinyl}-5,15-diphenylporphyrin (24): (Method III) Compound **23** (100 mg, 137 µmol), **17** (79 mg, 346 µmol), $Pd(PPh_3)_4$ (10 mg, 9 µmol, 3 mol-%), DME (10 mL), 1 M aqueous Na_2CO_3 (3 mL), 10 h reflux, adding H_2O (20 mL), extraction with CH_2Cl_2 (3 × 40 mL), and purification by flash chromatography (hexane/CH_2Cl_2 1:1; R_f = 0.47) gave **24** (106 mg, 113 µmol, 82%); purple solid; m.p. 205 °C (DSC peak onset). ^1H NMR (600 MHz): δ = 10.04 (s, 1 H, 15-H), 9.59 (d, $^3J_{16,17}$ = 15.7 Hz, 1 H, 16-H), 9.51 (d, $^3J_{8,7}$ = 4.6 Hz, 2 H, 8-H), 9.20 (d, $^3J_{13,12}$ = 4.5 Hz, 2 H, 13-H), 8.92 (d, $^3J_{12,13}$ = 4.5 Hz, 2 H, 12-H), 8.91 (d, $^3J_{7,8}$ = 4.6 Hz, 2 H, 7-H), 8.23–8.18 (m, 4 H, 3-H), 7.95 (s, 1 H, 24-H), 7.80–7.71 (m, 6 H, 1,2-H), 7.55 (d, $^3J_{17,16}$ = 15.7 Hz, 1 H, 17-H), 7.02 (d, $^4J_{27,29}$ = 1.7 Hz, 1 H, 27-H), 6.86 (d, $^4J_{20,18}$ = 1.7 Hz, 1 H, 20-H), 6.17 (d, $^4J_{29,27}$ = 1.7 Hz, 1 H, 29-H), 6.05 (d, $^4J_{18,20}$ = 1.7 Hz, 1 H, 18-H), 3.94 (d, $^3J_{30,31}$ = 6.5 Hz, 2 H, 30-H), 3.71 (d, $^3J_{36,37}$ = 6.5 Hz, 2 H, 36-H), 1.80–1.73 (m, 2 H, 37-H), 1.57–1.40 (m, 4 H, 31,38-H), 1.37–1.30 (m, 4 H, 39,40-H), 1.26–1.18 (m, 2 H, 32-H), 1.17–1.10 (m, 4 H, 33,34-H), 0.94–0.89 (m, 3 H, 41-H), 0.77–0.70 (m, 3 H, 35-H), –2.85 (s, 2 H, tautomeric NH) ppm. ^{13}C NMR (150 MHz): δ = 157.7 (s, C-28), 157.6 (s, C-19), 146.2 (br. signal, α-pyrrol-C-6,9,11,12), 141.8 (s, C-4), 137.1 (s, C-23), 136.6 (s, C-25), 135.8 (d, C-17), 135.0 (s, C-26), 134.7 (d, C-3), 133.38 (s, C-22), 133.36 (s, C-21), 131.4 (d, C-16), 131.0 (br. signal, β-pyrrol-C-7,12,13), 129.6 (br. signal, β-pyrrol-C-8), 127.7 (d, C-1), 126.8 (d, C-2), 122.2 (d, C-24), 119.8 (s, C-5), 119.2 (d, C-20), 117.1 (s, C-10), 116.7 (d, C-27), 104.8 (d, C-15), 98.5 (d, C-18), 96.9 (d, C-29), 70.1 (t, C-36), 70.0 (t, C-30), 31.6 (t, C-39), 31.4 (t, C-33), 29.2 (t, C-37), 29.0 (t, C-31), 25.7 (t, C-38), 25.5 (t, C-32), 22.6 (t, C-34), 22.4 (t, C-40), 14.1 (q, C-41), 13.9 (q, C-35) ppm. MS (EI): m/z (%) = 934/935/936/937 (100/60/35/16) $[M]^{+\cdot}$. HRMS (EI): calcd. for $C_{58}H_{54}N_4O_2S_3$ $[M]^{+\cdot}$ 934.3409; found 934.3416. FTIR: $\tilde{\nu}$ = 3307 (w), 3112 (w), 3054 (w), 2924 (w), 2855 (w), 1596 (w), 1552 (w), 1524 (m), 1455 (w), 1442 (w), 1403 (w), 1352 (m), 1238 (w), 1165 (m), 1065 (w), 1025 (w), 1001 (w), 971 (m), 956 (m), 928 (w), 847 (w), 788 (s), 722 (s) cm^{-1}. UV/Vis: λ (ε) = 654 (4700), 595 (sh.), 564 (12400), 518 (12300), 420 (183000) nm. $C_{58}H_{54}N_4O_2S_3$ (935.27): calcd. C 74.48, H 5.82, N 5.99, S 10.29; found C 74.12, H 5.89, N 5.99, S 10.06.

{10-{2-[3,4′′-Bis(hexoxy)-2,2′:5′,2′′-terthiophen-3′-yl]vinyl}-5,15-diphenylporphyrinato}cobalt(II) (25): (Method IB) Compound **24** (230 mg, 246 µmol), $Co(OAc)_2\cdot 4H_2O$ (720 mg, 2.89 mmol), DMF (15 mL), 2 h reflux, adding H_2O (60 mL), extraction with CH_2Cl_2 (5 × 100 mL), washing with brine (60 mL) and H_2O (5 × 100 mL) gave **25** (150 mg, 151 µmol, 61%); purple solid; m.p. 229 °C. MS (ESI MeOH/$CHCl_3$): m/z (%) = 991/992/993/994 (100/66/36/15) $[M^{+\cdot}/M + H^+]$. MS (APCI, $CHCl_3$): m/z (%) = 992/993/994/995 (34/100/68/38) $[M + H^+]$. HRMS (APCI, $CHCl_3$): calcd. for $C_{58}H_{53}N_4CoO_2S_3$ $[M + H^+]$ 992.2663; found 992.2642. FTIR: $\tilde{\nu}$ = 3113 (w), 3054 (w), 3023 (w), 2927 (m), 2853 (w), 1598 (w), 1527 (w), 1549 (m), 1529 (m), 1487 (w), 1467 (w), 1443 (w), 1386 (w), 1355 (m), 1209 (w), 1163 (m), 1068 (m), 1024 (w), 1000 (m), 951 (m), 854 (m), 816 (w), 792 (m), 778 (m), 749 (m), 722 (m) cm^{-1}. UV/Vis: λ (ε) = 578 (sh.), 533 (13500), 422 (136300) nm. $C_{58}H_{52}CoN_4O_2S_3$ (992.19): calcd. C 70.21, H 5.28, N 5.65, S 9.70; found C 70.14, H 5.37, N 5.77, S 9.33.

Supporting Information (see also the footnote on the first page of this article): Contains extra cyclic voltammograms (CV) of **4**, **8** and **12** as well as multisweep CVs of all compounds and CVs of NiDPP, ZnDPP, CuDPP and CoDPP. Furthermore $^1H/^{13}C$-NMR spectra and the nomenclature of all carbons and hydrogens for signal assignment are included.

Acknowledgments

We thank the Bundesministerium für Bildung und Forschung (BMBF) and Deutsches Zentrum für Luft und Raumfahrt (DLR) (FKZ 01BI565) for financial support.

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Received: October 30, 2009 (revised May 4, 2010)