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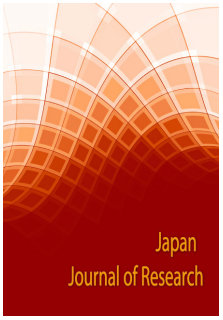

Synthesis of β-Hexasubstituted Porphyrins by *Vicarious Nucleophilic Substitution of Hydrogen*. Closing Research

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Abstract

meso-Tetraarylporphyrin chelates in the electrophilic reactions with nitric acid, under optimized conditions, can give mainly β,β,β-trinitro-substituted moieties. These intermediates (Cu^{2+}- and Zn^{2+}-derivatives; obtained in overall yields of up to 38%), upon the reaction with carbanions bearing a leaving group X at the reactive centre afford the target products, the ones of vicarious nucleophilic substitution of hydrogen (VNS). This approach allows the synthesis of hydrophilic or amphiphilic porphyrin derivatives exhaustively β-substituted in three pyrrole rings that seem to be potential agents in anticancer photodynamic therapy (PDT). The above two-step procedure including very attractive VNS reaction leads to moieties practically unavailable by alternative methods.

Introduction

Porphyrin derivatives are compounds of significant importance, intensively studied in the past decades [1]. They can be used as valuable materials in many areas. This particularly applies to highly functionalized porphyrins. Among others, the introduction of various substituents to the β-positions of the macrocycle opens an access to the tuning of the electronic and, in turn, physico-chemical characteristics of the obtained systems [2]. In this context, it needs to be highlighted that strong electron-deficient β-substituted porphyrins (such as those substituted with NO_2 groups) are in the spotlight, as they reveal very interesting properties. For example, electron-withdrawing β-substituents significantly affect the electronic structure of porphyrins [3].

It is known that the nitro group, connected with the aromatic π-system, is a powerful electron-withdrawing function that influences the reactivity of these compounds. In such electron-deficient arenes, halogens (or other nucleophugal groups) are readily replaced by nucleophiles *via* S_NAr or an addition–elimination mechanism [4]. On the other hand, a variety of carbanions, *N*-anions, *O*-anions, and other nucleophilic agents can add at the position *ortho*- or *para*- to the nitro group (occupied by hydrogen), thus giving σ^H-adducts, that upon various transformations lead to products of substitution of hydrogen [5]. Therefore, the NO_2 group is widely used in the field of organic synthesis to solve a variety of current problems.

Results and Discussion

Easily available parent *meso*-tetraarylporphyrins, after complexation to copper chelates, have been reacted with yellow fuming nitric acid (d = 1.52). These electrophilic reactions carried out in chloroform at room temperature, under optimized conditions can give selectively β,β,β-trinitro-substituted derivatives (usually two or three isomers of the above complexes) [6]. The obtained intermediates (*e.g.*, Cu^{2+}-complexes), may be excellent starting material for reactions with carbanions.

Among other reactions with carbanions, there is a *vicarious nucleophilic substitution of hydrogen* (VNS) that involves species bearing a leaving group X at the reactive centre. It is very good tool for functionalization of nitroarenes, nitro-heteroarenes, and many other heteroaromatic compounds [5]. In the last two decades it was also applied for the porphyrin macrocycle, thus allowing the synthesis of highly decorated moieties: in *meso*-aryl rings and at the peripheral positions β- – in NO_2-activated systems and/or in some derivatives active by themselves [7,8]. It is a process of general character.

This approach was used in our laboratory for preparation of di-, tri-, and tetrasubstituted porphyrins at the β-positions, affording the respective products with good or very good yield [9-14]. In the recent past it was communicated that synthesis penta- and hexa-derivatized products can also be realized [15]. A paper dealing with some preliminary attempts using carbanions of halomethyl-aryl sulphones was

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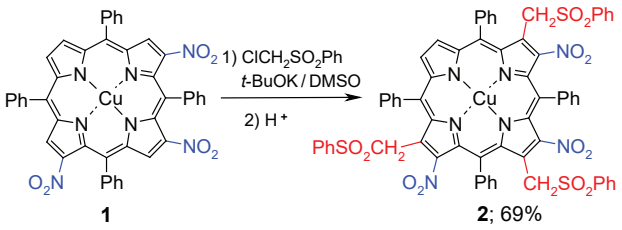
published lately in *Organic Communications* [15] (one of the products obtained is shown below; Scheme 1). Substrates for the latter compounds were isomers of β,β,β-trinitro-porphyrin complexes, described in our previous paper [6]. They were used (by applying VNS reaction) for nucleophilic transformation leading to the desired porphyrinyl macrocycles. The target moieties were sulphur-decorated architectures from one side (marked with red colour), while the parent nitro-substituted porphyrin substrate was based on 3,7,12-trinitro-pattern (NO_2 groups marked with blue colour). Herein, we would like to broaden the spectrum of substituents, as well as to test other porphyrinates: 2,7,13-trinitro– and (2,8,12-trinitro-5,10,15,20-tetraphenylporphyrinato)copper(II). It is worth mentioning that not only copper complexes were studied but also a zinc one.



***Scheme 1**. VNS synthesis of β-hexasubstituted porphyrins (an example taken from the literature [15]).*

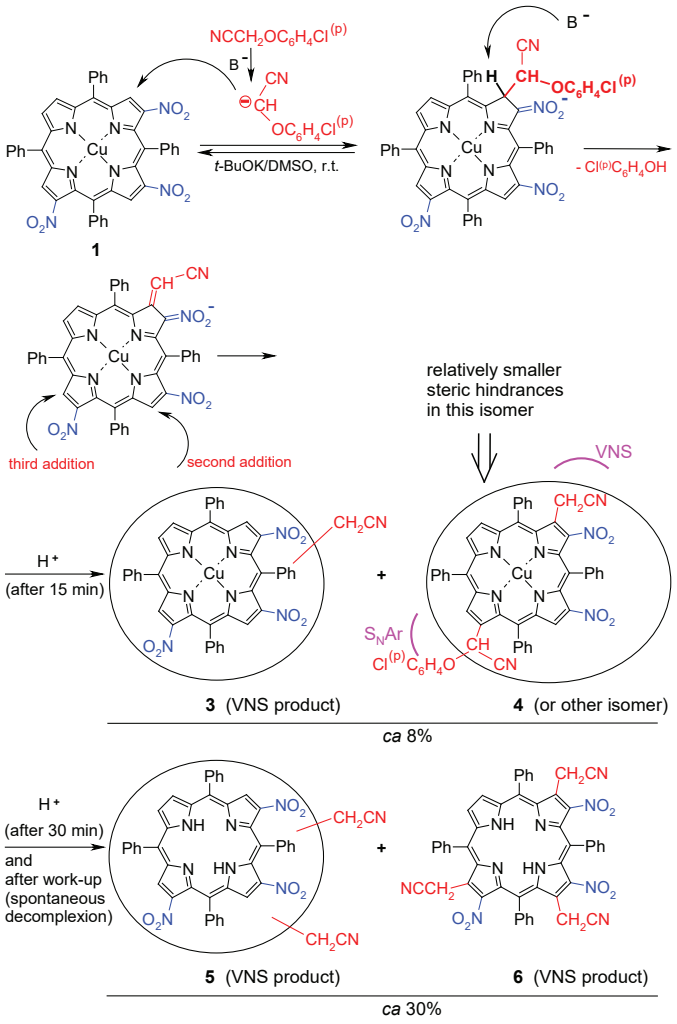
3,7,12-Trinitro-porphyrin Cu(II)–Complex (Reactions with *para*-Chlorophenoxy-acetonitrile)

In this work, we would like to finally determine the scope and limitations of the VNS methodology for the synthesis of new hexasubstituted porphyrins that have attractive and/or easily transformable functional groups. As substrates were used herein highly electrophilic β,β,β-trinitro-substituted *meso*-tetraphenyl-porphyrinates whose synthesis has recently been developed in our laboratory [6]. In the last year we also published a preliminary communication dealing with the VNS reactions of copper chelates (mentioned above) with α-halomethyl–aryl sulphones [15]. Now, we would like to extend this methodology to other trinitro-porphyrin complexes, namely zinc ones or compounds having a different substitution pattern of the NO_2 groups, as well as other carbanions.

In the reaction of trinitroporphyrinate **1** with more nucleophilic carbanion of *para*-chlorophenoxy-acetonitrile (under conditions: *t*-BuOK/DMSO, r.t., 0.5 h) we observed on TLC formation of several porphyrin compounds. In one isolated fraction the desired hexasubstituted product was found (yield *ca* 30%). We postulated its structure on the basis of MS spectrum, and it was identified as decomplexed form **6** (Scheme 2). Unfortunately, the mixture was inseparable.

In summary, the prolonged reaction time (0.5 h) favours the formation of exhaustively hexasubstituted product **6**. The loss of readily released Cu^{2+} cation probably occurred during the work-up that is possible for labile copper(II) complex. It is difficult to achieve a better result in this case due to limited chemical robustness of the product (in the presence of a base). Its degradation is starting to significantly increase with time. It is worth noting that the reaction carried out in a shorter time (15 min) leads mainly to monosubstituted moiety **3**.

During the MS measurements, other molecular or pseudo-molecular ions of various individua were also detected in the spectra of the above reaction mixtures, that can be assigned to the appropriate products, *e.g.* **3** (monosubstitution of hydrogen),



***Scheme 2.** VNS mechanism for the reaction of porphyrin **1** with para-chlorophenoxy-acetonitrile (followed by decomplexion of the products).*

4 (monosubstitution of hydrogen in conjunction with S_NAr of one NO_2 group), or **5** (double substituted VNS product). Their identity was confirmed by the composition of ions observed in the MS spectra. These types of products are very attractive as the CN group can be transformed into other polar functionalities, important from the PDT point of view, *e.g.* CO_2H, $CONH_2$, CH_2NH_2, CHO, CH_2OH, etc. They make the moiety more soluble in physiological milieu.

We observed that with some carbanions of strong nucleophilicity, *e.g.* methylenic carbanion $(PhS)(Ph)CH^-$, the reaction doesn't work, probably due to low rate of elimination of thiophenyl group (PhS).

Reaction of 3,7,12-Trinitro-porphyrin Cu(II)–Complex (**1**) with *n*-Butyl–Trifluoromethyl Sulphone

In the next step we attempted to introduce at the β-positions of the porphyrin skeleton a simple alkyl groups. In this case the carbanion used ought to have only one functional group which plays a role of activating/stabilizing carbanion group from one side and a leaving group from the other. Such carbanions can be generated from alkyl sulphonium and sulphoxonium salts (Corey-Chaykovsky reagents) [16,17], alkyl-phenyl selenones ($PhSeO_2CH_2R$) [18], alkyl sulphones and sulphonates [19], or alkyl-perfluoromethyl sulphones [20]. These reagents were

utilized for direct alkylation and cyclopropanation of highly electrophilic and stable aromatic systems [17,19-27]. One of the latter ($C_3H_7CH_2SO_2CF_3$) has already been reported as convenient substrate in VNS reaction [20]; there it was successfully used for alkylation. But not in our case!

Herein, in the reaction of trinitro-isomer **1** with *n*-butyl–trifluoromethyl sulphone several products were observed on TLC. This mixture was inseparable. Using MS analysis we didn't find ions originating from the desired product (**9**; see Fig. 1). Some ions suggested ONSH processes [28], some S_NAr substitution [4]; all of them were rather an effect of partial degradation of the porphyrin system. Thus, the first product was mono-substituted ONSH moiety (**7**), while the second one was rather unexpected derivative. On the basis of the MS spectrum, we proposed for it a structure of double S_NAr-substituted compound (**8**).

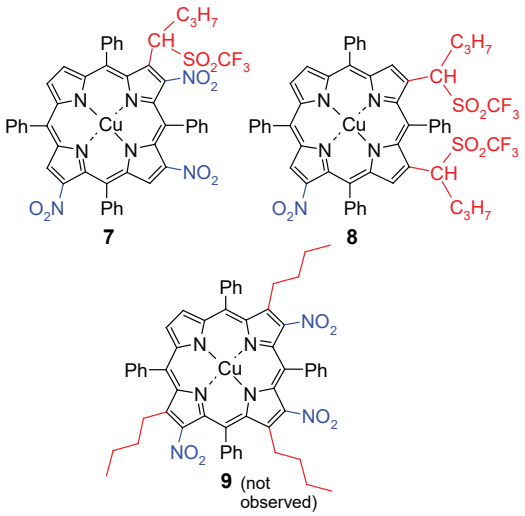


Figure 1. *The products identified in the post-reaction mixtures of the reaction of [3,7,12-trinitro-5,10,15,20-tetraphenylporphyrinato]copper(II) (**1**) with n-butyl–trifluoromethyl sulphone ($C_4H_9SO_2CF_3$) (**7**, **8** – possible other isomers).*

We can conclude herein that β,β,β-trinitro-porphyrin derivative was too reactive towards the more nucleophilic carbanions, bearing moderate leaving groups (such as OAr, SO_2CF_3, SPh). This affects the progressive fast degradation of the porphyrin substrate. Moreover, in the reaction with $C_3H_7CH_2SO_2CF_3$ the desired trialkylated product **9** was not formed at all. Therefore, the studies concerning this approach to the synthesis of β-hexa-substituted porphyrins have been suspended.

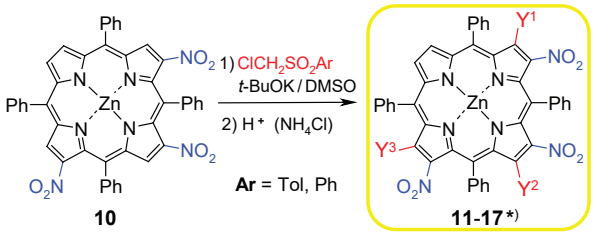
Reactions of [3,7,12-Trinitro-5,10,15,20-tetraphenylporphyrinato]zinc(II) with Chloromethyl-Aryl Sulphones

Finally, carbanions of chloromethyl-aryl sulphones (very often used in VNS) were reacted with [3,7,12-trinitro-5,10,15,20-tetraphenylporphyrinato]zinc(II) (**10**). These types of complexes are very convenient due to their diamagnetic properties. Thus, the reaction(s) could be followed by NMR spectroscopy. Earlier (and partly in this article), we demonstrated the route to hexa-substituted at the β-positions porphyrin derivatives in tandem electrophilic nitration/VNS substitution reaction. Mostly they were copper(II) chelates. We wanted to extend this methodology on other porphyrinates, thus the above zinc(II) complex was taken to the research.

In the first experiment between chloromethyl–*para*-tolyl sulphone and porphyrinate **10** (under conditions: *t*-BuOK/DMSO, r.t.) after 0.5 h of stirring, the substrate disappeared resulted in the formation of two products (TLC control). They were identified by MS method as two isomers (of three possible) of pentasubstituted derivatives [*m/z* = 1170, $(M+Na)^+$; defined herein as **11** and **12**, see Scheme 3]. Their molecular formulae (and masses) were confirmed by HR measurements for pseudo-molecular $(M+Na)^+$ ions. Both were isolated chromatographically and characterized, however the structures couldn't be assigned to the corresponding isomers. The total yield of the reaction was moderate (38%). Prolongation of the reaction time did not result in a formation of exhaustively substituted product **13**, probably due to its instability; in the strong basic reaction conditions it exists in a trianionic form that is easily decomposed. Therefore, only traces of **13** were observed.

How to explain this result? Especially in the context of the fact that we have earlier obtained these types of hexasubstituted products for copper complexes [15]. First of all, it should be noted that for the latter we also observed easy degradation of the target species, existing in trianionic forms under the reaction conditions. Thus, the reaction time should not be too long. Similarly herein, prolongation of the reaction time resulted in the formation of the desired product on the one hand, and its simultaneous degradation on the other. With the difference that in the case of more labile zinc chelate, the degradation was faster. The results obtained are summarized in Scheme 3.

Similar results were observed for the carbanion of $ClCH_2SO_2Ph$ except for the yield that was much higher in this case (61%). Interestingly, the formation of all three pentasubstituted isomers (**14-16**) was detected. Although their isolation and purification was not a trivial problem, an analytical samples could be isolated chromatographically and characterized.



11,12: Y^1,Y^2 or Y^1,Y^3 or Y^2,Y^3 = CH_2SO_2Tol (two isomers); 38%

13: Y^1,Y^2,Y^3 = CH_2SO_2Tol (traces)**)

14-16: Y^1,Y^2 or Y^1,Y^3 or Y^2,Y^3 = CH_2SO_2Ph (three isomers); 61%

17: Y^1,Y^2,Y^3 = CH_2SO_2Ph (traces)**)

*) unless otherwise stated, Y^i = H; i = 1, 2, 3

**) not isolated from the post-reaction mixture

Scheme 3. *VNS reactions of [3,7,12-trinitro-5,10,15,20-tetraphenylporphyrinato]zinc(II) (**10**) with chloromethyl-aryl sulphones.*

Functionalization of Other β,β,β-Trinitro-porphyrinates

In this part of the studies we involved two other β,β,β-trinitro-porphyrin Cu(II)-complexes into reactions with carbanions of α-chloroalkyl sulphones, namely (2,7,13-trinitro-5,10,15,20-tetraphenylporphyrinato)copper(II) (**18**) and (2,8,12-trinitro-5,10,15,20-tetraphenylporphyrinato)copper(II) (**19**), that had a different substitution pattern of the NO_2 groups at the β-positions.

It was the most successful part of the research; in the reactions of the above porphyrinates with chloromethyl-aryl sulphones the products were formed in high yield (up to 94%). Moreover, in this case, the moieties exhaustively substituted in

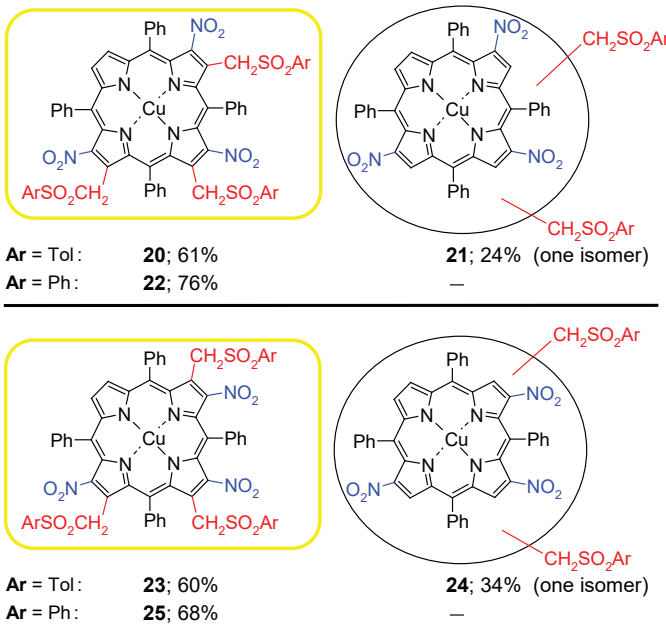


Figure 2. *Products obtained in the reactions of copper(II)-porphyrinates **18** and **19** with chloromethyl–para-tolyl sulphone and chloromethyl-phenyl sulphone.*

three pyrrole rings predominated (61-76%), sometimes being here the only derivatives (*e.g.*, **22**, **25**). Therefore, the amounts of the pentasubstituted byproducts **21**/**24** (and others) were significantly decreased or not observed at all (in both cases only one additional product was formed of the three possible individua). We confirmed their molecular and pseudo-molecular masses by HR-MS or by comparing the theoretical and experimental isotope patterns for diagnostic ions. All the results were summarized in Figure 2.

Conclusion

The studies described in this paper focused on the possibility of synthesizing β-multisubstituted porphyrins. As substrates, copper(II) and zinc(II) trinitro-TPP complexes were used. On the other hand, for the reactions we have selected carbanions of higher nucleophilicity, for example *para*-chlorophenoxy-acetonitrile or *n*-butyl–trifluoromethyl sulphone. In both cases, among others, in the reactions with these strong nucleophilic carbanions S_NAr products were observed; and this substitution competed with VNS substitution.

It can be easily rationalized. An addition to carbon atom bearing hydrogen is faster, however β-elimination, due to decreased ability to leave of poor leaving group (OAr, SO_2CF_3), is slower or does not occur at all. Therefore, the equilibrium allows the secondary addition to β-position occupied by NO_2 group to give S_NAr product. The latter addition is activated by two remaining NO_2 groups. This is a limitation for the synthesis of the title compounds. However, we managed to obtain some amounts of the desired hexasubstituted products. It should be noted that they can be obtained easily with carbanions of moderate nucleophilicity [15]. Interestingly, for zinc chelate the reactions did not lead to the formation of the exhaustively hexasubstituted products. They were observed in small amounts only due to limited robustness of the target moieties. The most successful results came from the reactions of 2,7,13-trinitro- and 2,8,12-trinitro-porphyrin copper(II)-complexes (having a different substitution pattern of the NO_2 groups) with chloromethyl-aryl sulphones. In this case, the yields reached up to 94% of the isolated products.

This type of functionalization gave rise to hydrophilic or amphiphilic compounds with five and six polar groups on the rim of the core ring (*e.g.* NO_2, CH_2CN, CH_2SO_2R). They are of interesting value and can be considered as intermediates for further transformations. This two-step procedure including very attractive VNS reaction leads to porphyrin derivatives practically unavailable by alternative methods that seem to be potential agents in anticancer photodynamic therapy (PDT).

Experimental

^{1}H NMR spectra were recorded with a Varian MR-400 spectrometer, operating at 400 MHz. Coupling constants *J* are expressed in hertz [Hz]. Mass spectra were measured with a GCT Premier (Waters, FD-TOF) spectrometer (FD method) and MARINER (PerSeptive Biosystems, ESI-TOF) spectrometer (ESI method); *m/z* intensity values for peaks are given as a % of relative intensity. UV-vis spectra were measured with a Metertech SP-8001 spectrophotometer. TLC analysis was performed on aluminium foil plates pre-coated with silica gel (60 F-254, Merck AG). All the products were isolated by column chromatography (silica gel, 230-400 mesh; Merck AG). Some compounds were rechromatographed on preparative TLC plates (silica gel, 60 F-254, 2 mm and 0.5 mm; Merck AG). Molecular formulas of new compounds were confirmed by HR-MS (ESI method), and by comparing the isotope molecular patterns (theoretical and experimental).

All the reactions were carried out in light-shielded flasks equipped with a septum. Preparation of starting β,β,β-trinitro-5,10,15,20-tetraphenylporphyrinates (**1**,**10**,**18**, and **19**) was described in the earlier literature [6]. Carbanion precursors were also obtained according to known procedures: *para*-chlorophenoxy-acetonitrile [29], *n*-butyl–trifluoromethyl sulphone [30], benzyl-phenyl sulphide ($PhCH_2SPh$) [31], α-chloromethyl–*para*-tolyl sulphone [32], and α-chloromethyl–phenyl sulphone [33].

Reaction of [3,7,12-Trinitro-5,10,15,20-tetraphenylporphyrinato] copper(II) (**1**) with *para*-Chlorophenoxy-acetonitrile

In a round-bottomed, light-shielded flask [3,7,12-trinitro-5,10,15,20-tetraphenylporphyrinato]copper(II) (**1**; 65 mg, 0.080 mmol) was dissolved in anhydrous DMSO (20 mL). The mixture was stirred for *ca* 30 min due to solubility problem of porphyrinate. To this mixture *para*-chlorophenoxy-acetonitrile (217 mg, 1.30 mmol) was added in one portion. After 5 min of stirring, the solution obtained was dropped *via* syringe (under argon) to a stirred *t*-BuOK (217 mg, 1.93 mmol) in anhydrous DMSO (10 mL) over a period of *ca* 5 min. After the next 5 min of stirring an additional portion of *t*-BuOK (100 mg, 0.89 mmol) in DMSO (2 mL) was added.

The reaction was carried out at room temperature, under argon, for 15-30 min (TLC control). Then, the mixture was poured into aqueous 3% NH_4Cl containing ice (400 mL). The precipitate was filtered, washed with water (200 mL), and then dissolved in $CHCl_3$ (45 mL). After drying with anhydrous $MgSO_4$ and evaporation of the solvent, the products were isolated by column chromatography (eluent: $CHCl_3$ to $CHCl_3$/MeOH, 100:1) to give: (a) reaction time – 15 min; a mixture of [β-cyanomethyl-3,7,12-trinitro-5,10,15,20-tetraphenylporphyrinato]copper(II) (**3**) and product **4** ([β,β-$(NO_2)_2$-β-(CH_2CN)-β-{CH(CN)

($OC_6H_4Cl^{(p)}$)}-TPP]Cu(II), yield of both products – 5.8 mg, *ca* 8%); (b) reaction time – 30 min; a mixture containing mainly products **5** and **6**, approximate yield of both products – 20.3 mg, *ca* 30%. Postulated formulas **3**, **4**, and **5** can represent one or more possible isomers.

(a):

[β-Cyanomethyl-3,7,12-trinitro-5,10,15,20-tetraphenylporphyrinato] copper(II) (**3**) (in the mixture **3**+**4**): MS (FD), *m/z* (% rel. int.): 854 (7), 853 (9), 852 (28), 851 (52), 850 (62), 849 (100) [isotope M^+ and $(M+H)^+$]. MS (ESI), *m/z* (% rel. int.): 876 (9), 875 (27), 874 (61), 873 (54), 872 (100) [isotope $(M+Na)^+$]; 854 (8), 853 (9), 852 (21), 851 (40), 850 (34), 849 (62) [isotope M^+]. HR-MS (ESI): calcd for $C_{46}H_{26}N_8O_6CuNa$ [$(M+Na)^+$] – 872.1169; found – 872.1167.

Product **4** (in the mixture **3**+**4**): MS (FD), *m/z* (% rel. int.): 975 (6), 974 (9), 973 (10), 972 (35), 971 (46), 970 (32), 969 (52) [isotope M^+]. MS (ESI), *m/z* (% rel. int.): 998 (3), 997 (6), 996 (12), 995 (17), 994 (30), 993 (19), 992 (33) [isotope $(M+Na)^+$]; 974 (3), 973 (6), 972 (10), 971 (14), 970 (12), 969 (15) [isotope M^+]. HR-MS (ESI): calcd for $C_{54}H_{31}N_8O_5CuNaCl$ [$(M+Na)^+$] – 992.1300; found – 992.1291.

(b):

β,β-Bis(cyanomethyl)-3,7,12-trinitro-5,10,15,20-tetraphenylporphyrin (**5**) (in the mixture **5**+**6**): MS (ESI), *m/z* (% rel. int.): 817 (22), 816 (40), 815 (67), 814 (56), 813 (87), 812 (40), 811 (59) [isotope $(M–O)^+$].

2,8,13-Tris(cyanomethyl)-3,7,12-trinitro-5,10,15,20-tetraphenylporphyrin (**6**) (in the mixture **5**+**6**): MS (ESI), *m/z* (% rel. int.): 832 (15), 831 (29), 830 (37), 829 (71), 828 (63), 827 (100), 826 (49), 825 (81) [isotope $(MH–CN–O)^+$]; 802 (43), 801 (85), 800 (52), 799 (97), 798 (37), 797 (50) [isotope $(MH–CH_2CN–NO)^+$].

Reaction of [3,7,12-Trinitro-5,10,15,20-tetraphenylporphyrinato] copper(II) (**1**) with *n*-Butyl–Trifluoromethyl Sulphone

In a round-bottomed light-shielded flask, NaH (39 mg, 0.98 mmol; 60% oil dispersion, initially washed with hexane to remove mineral oil) was suspended in anhydrous DMF (2.4 mL). Then, *n*-butyl–trifluoromethyl sulphone (105 mg, 0.55 mmol) in DMF (2.4 mL) was dropped *via* syringe (under argon). After 5 min, [3,7,12-trinitro-5,10,15,20-tetraphenylporphyrinato]copper(II) (**1**; 30 mg, 0.037 mmol) in DMF (1.5 mL) was added in one portion.

The reaction was carried out at room temperature, under argon, for 25 min (TLC control). Then, the mixture was poured into aqueous 3% NH_4Cl containing ice (100 mL). The precipitate was filtered, washed with water (300 mL), and dried. The crude post-reaction mixture consists of many products (several inseparable spots on TLC plates were observed). It was analyzed by MS spectrometry. Postulated products: **7**, **8**.

Product **7**: MS (ESI), *m/z* (% rel. int.): 1004 (5), 1003 (12), 1002 (33), 1001 (61), 1000 (69), 999 (100), 998 (21) [isotope M^+ and $(M+H)^+$]; 965 (5), 964 (12), 963 (22), 962 (24), 961 (40), 960 (18) [isotope $(M–2×F)^+$]; 935 (11), 934 (21), 933 (24), 932 (39), 931 (15), 930 (15), 929 (18) [isotope $(M–CF_3)^+$].

Product **8**: MS (ESI), *m/z* (% rel. int.): 964 (12), 963 (22), 962 (24), 961 (40), 960 (18), 959 (27), 958 (6) [isotope $(M–2×CF_3)^+$]. The theoretical and experimental isotope patterns for the ion *m/z*=958 are not identical due to overlapping with ion *m/z*=960 [$(M–2×F)^+$] from product **7**.

Reaction of [3,7,12-Trinitro-5,10,15,20-tetraphenylporphyrinato] zinc(II) (**10**) with Chloromethyl–*para*-Tolyl Sulphone

In a round-bottomed light-shielded flask, [3,7,12-trinitro-5,10,15,20-tetraphenylporphyrinato]zinc(II) (**10**; 60 mg, 0.074 mmol) was dissolved in anhydrous DMSO (20 mL). The mixture was stirred for *ca* 30 min due to solubility problem of porphyrinate. To this mixture, chloromethyl–*para*-tolyl sulphone (210 mg, 1.03 mmol) was added in one portion. After 5 min of stirring, the solution obtained was dropped *via* syringe (under argon) to a stirred *t*-BuOK (210 mg, 1.87 mmol) in anhydrous DMSO (10 mL) over a period of *ca* 5 min. The reaction was continued at room temperature under argon. After the next 5 min of stirring an additional portion of *t*-BuOK (200 mg, 1.78 mmol) in DMSO (1 mL) was added. The reaction was carried out for 25-30 min (TLC control). Then, the mixture was poured into aqueous 3% NH_4Cl containing ice (350 mL). The precipitate was filtered, washed with water (400 mL), dried, and then dissolved in $CHCl_3$ (45 mL). The solvent was evaporated and the products were isolated by column chromatography (eluent: $CHCl_3$/MeOH, 100:1) followed by purification on preparative TLC (eluent: $CHCl_3$/MeOH, 100:1) to give two isomers (of three theoretically possible) of [3,7,12-trinitro-β,β-bis{(toluene-4-sulphonyl)methyl}-5,10,15,20-tetraphenylporphyrinato] zinc(II) (**11**/**12**): a) isomer **11**, 16.8 mg (20%); b) isomer **12**, 15.1 mg (18%).

In the MS spectrum of crude post-reaction mixture the ions of hexasubstituted product (**13**; $C_{68}H_{49}N_7O_{12}S_3Zn$) were also found. This was formed in small amounts and it was not possible to isolate it from the mixture.

[3,7,12-Trinitro-β,β-bis{(toluene-4-sulphonyl)methyl}-5,10,15,20-tetraphenylporphyrinato]zinc(II) (**11**/**12**):

Isomer **11**: R_f=0.45 ($CHCl_3$/MeOH, 100:1). m.p. > 300ºC. ^{1}H NMR ($CDCl_3$, 400 MHz); δ [ppm]: 8.63 (broad s, 2H, $H^β$-pyrrole), 8,57 (s, 1H, $H^β$-pyrrole), 8.43–8.04 (m, 8H, H-Ph), 7.90–7.62 (m, 12H, H-Ph), 7.17–6.93 (m, 8H, H-Tol), 5.44–5.22 (m, 4H, 2×CH_2), 2.33 (apparent s, 6H, 2×CH_3). UV-vis ($CHCl_3$); $λ_{max}$ [nm] (log ε): 652 (3.99), 592 (3.66), 469 (4.71; Soret band), 351.5 (4.26). MS (ESI), *m/z* (% rel. int.): 1178 (8), 1177 (11), 1176 (20), 1175 (38), 1174 (67), 1173 (63), 1172 (94), 1171 (75), 1170 (100) [isotope $(M+Na)^+$]. HR-MS (ESI): calcd for $C_{60}H_{41}N_7O_{10}S_2ZnNa$ [$(M+Na)^+$] – 1170.1545; found – 1170.1537.

Isomer **12**: R_f=0.50 ($CHCl_3$/MeOH, 100:1). m.p. > 300ºC. ^{1}H NMR ($CDCl_3$, 400 MHz); δ [ppm]: 8.62 (broad s, 2H, $H^β$-pyrrole), 8.57 (s, 1H, $H^β$-pyrrole), 8.38–8.12 (m, 8H, H-Ph), 7.88–7.60 (m, 12H, H-Ph), 7.18–6.90 (m, 8H, H-Tol), 5.44–5.21 (m, 4H, 2×CH_2), 2.32 (s, 6H, 2×CH_3). UV-vis ($CHCl_3$); $λ_{max}$ [nm] (log ε): 683.5 (4.03), 611 (3.81), 476 (4.94; Soret band), 347.5 (4.40). MS (ESI), *m/z* (% rel. int.): 1177 (6), 1176 (14), 1175 (33), 1174 (62), 1173 (71), 1172 (100), 1171 (75), 1170 (84) [isotope $(M+Na)^+$]. HR-MS (ESI): calcd for $C_{60}H_{41}N_7O_{10}S_2ZnNa$ [$(M+Na)^+$] – 1170.1545; found – 1170.1537.

[3,7,12-Trinitro-2,8,13-tris{(toluene-4-sulphonyl)methyl}-5,10,15,20-tetraphenylporphyrinato]zinc(II) (**13**): MS (ESI), *m/z* (% rel. int.): 1343 (3.9), 1342 (5.7), 1341 (5.7), 1340 (7.5), 1339 (6.5), 1338 (7.5) [isotope $(M+Na)^+$].

Reaction of [3,7,12-Trinitro-5,10,15,20-tetraphenylporphyrinato] zinc(II) (**10**) with Chloromethyl-Phenyl Sulphone

In a round-bottomed, light-shielded flask, [3,7,12-trinitro-5,10,15,20-tetraphenylporphyrinato]zinc(II) (**10**; 30 mg, 0.037 mmol) was dissolved in anhydrous DMSO (10 mL). The mixture was stirred for *ca* 30 min due to solubility problem of porphyrinate. To this mixture, chloromethyl-phenyl sulphone

(123 mg, 0.65 mmol) was added in one portion. The solution obtained was dropped *via* syringe (under argon) to a stirred *t*-BuOK (96 mg, 0.86 mmol) in anhydrous DMSO (10 mL) over a period of *ca* 5 min. The reaction was continued at room temperature under argon. After the next 5 min of stirring an additional portions of carbanion precursor (54 mg, 0.28 mmol) and *t*-BuOK (96 mg, 0.86 mmol) in small amounts of DMSO (1 mL + 1 mL) were added. The reaction was carried out for 25-30 min (TLC control). Then, the mixture was poured into aqueous 3% NH_4Cl containing ice (300 mL). The precipitate was filtered, washed with water (350 mL), dried, and then dissolved in a small amount of $CHCl_3$. The products were isolated on preparative TLC plates (eluent: $CHCl_3$/MeOH, 250:1) to afford isomers of [3,7,12-trinitro-β,β-bis{(phenylsulphonyl)methyl}-5,10,15,20-tetraphenylporphyrinato]zinc(II): a) a mixture of two isomers **14-15**; 15.0 mg (36%); an analytical samples of these isomers **14** and **15** were chromatographically isolated from the mixture and characterized; on the basis of these data, the structures couldn't be assigned to individual isomers; b) isomer **16** (single product); 10.2 mg (25%). Total yield of all three isomers – 61%.

In the MS spectrum of crude post-reaction mixture the ions originating from hexasubstituted product (**17**; $C_{65}H_{43}N_7O_{12}S_3Zn$) were also found. It was formed in small amounts (not isolated from the mixture).

[3,7,12-Trinitro-β,β-bis{(phenylsulphonyl)methyl}-5,10,15,20-tetraphenylporphyrinato]zinc(II) (**14-16**):

Isomer **14**: m.p. > 300ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm]: 8.98 (s, 1H, H$^{\beta}$-pyrrole), 8.69 and 8,59 (AB, J = 4.6 Hz 2H, H$^{\beta}$-pyrrole), 8.31–8.08 (m, 8H, H-Ph), 7.84–7.51 (m, 12H, H-Ph), 7.46–7.29 (m, 4H, H-SO_2Ph), 7.18–6.84 (m, 6H, H-SO_2Ph), 5.41–5.33 (m, 4H, 2×CH_2). UV-vis ($CHCl_3$); λ_{max} [nm] (log ε): 690.5 (3.94), 608.5 (3.67), 479 (4.89; Soret band), 349.5 (4.30). MS (ESI), *m/z* (% rel. int.): 1148 (36), 1147 (48), 1146 (82), 1145 (71), 1144 (98), 1143 (81), 1142 (100) [isotope $(M+Na)^+$]; 1125 (24), 1124 (36), 1123 (41), 1122 (45), 1121 (51), 1120 (53), 1119 (40) [isotope M^+ and $(M+H)^+$]. HR-MS (ESI): calcd for $C_{58}H_{38}N_7O_{10}S_2Zn$ [$(M+H)^+$] – 1120.1413; found –1120.1414. LR-MS (ESI): calcd for $C_{58}H_{37}N_7O_{10}S_2ZnNa$ [$(M+Na)^+$] – 1142.12; found – 1142.08. The molecular formula was also confirmed by comparing the theoretical and experimental isotope pattern for the $(M+Na)^+$ ion ($C_{58}H_{37}N_7O_{10}S_2ZnNa$) – it was found to be identical within the experimental error limits.

Isomer **15**: m.p. > 300ºC. ^{1}H NMR ($CDCl_3$, 400 MHz); δ [ppm]: 8,91 (s, 1H, H$^{\beta}$-pyrrole), 8.66 and 8.62 (AB, J = 4.7 Hz, 2H, H$^{\beta}$-pyrrole), 8.43–8.08 (m, 8H, H-Ph), 7.88–7.62 (m, 12H, H-Ph), 7.46–7.32 (m, 4H, H-SO_2Ph), 7.18–7.05 (m, 6H, H-SO_2Ph), 5.39–5.32 (m, 4H, 2×CH_2). UV-vis ($CHCl_3$); λ_{max} [nm] (log ε): 691.5 (3.81), 628 (3.60), 480.5 (4.75; Soret band), 346 (4.17). MS (ESI), *m/z* (% rel. int.): 1148 (36), 1147 (48), 1146 (82), 1145 (71), 1144 (98), 1143 (81), 1142 (100) [isotope $(M+Na)^+$]; 1125 (24), 1124 (36), 1123 (41), 1122 (45), 1121 (51), 1120 (53), 1119 (40) [isotope M^+ and $(M+H)^+$]. HR-MS (ESI): calcd for $C_{58}H_{38}N_7O_{10}S_2Zn$ [$(M+H)^+$] – 1120.1413; found –1120,1414. LR-MS (ESI): calcd for $C_{58}H_{37}N_7O_{10}S_2ZnNa$ [$(M+Na)^+$] – 1142.12; found – 1142.08. The molecular formula was also confirmed by comparing the theoretical and experimental isotope pattern for the $(M+Na)^+$ ion ($C_{58}H_{37}N_7O_{10}S_2ZnNa$) – it was found to be identical within the experimental error limits.

Isomer **16**: m.p. > 300ºC. ^{1}H NMR ($CDCl_3$, 400 MHz); δ [ppm]: 8.68 (s, 1H, H$^{\beta}$-pyrrole), 8.63 and 8.55 (AB, J = 4.8 Hz 2H, H$^{\beta}$-pyrrole), 8.36–8.10 (m, 8H, H-Ph), 7.86–7.63 (m, 12H, H-Ph), 7.55–7.45 (m, 4H, H-SO_2Ph), 7.28–7.07 (m, 6H, H-SO_2Ph), 5.40–5.33 (m, 4H, 2×CH_2). UV-vis ($CHCl_3$); λ_{max} [nm] (log ε): 708 (3.87), 634 (3.65), 477 (4.81; Soret band), 352 (4.20). MS (ESI), *m/z* (% rel. int.): 1148 (14), 1147 (33), 1146 (63), 1145 (69), 1144 (100) 1143 (77), 1142 (93) [isotope $(M+Na)^+$].

[3,7,12-Trinitro-2,8,13-tris{(phenylsulphonyl)methyl}-5,10,15,20-tetraphenylporphyrinato]zinc(II) (**17**): MS (ESI), *m/z* (% rel. int.): 1300 (5.7), 1299 (6.1), 1298 (8.5), 1297 (7.3), 1296 (9.4) [isotope $(M+Na)^+$]; 1200 (17), 1199 (15), 1198 (23), 1197 (18), 1196 (25) [isotope $(M–Ph)^+$].

Reaction of [2,7,13-Trinitro-5,10,15,20-Tetraphenylporphyrinato] copper(II) (**18**) with Chloromethyl–*para*-Tolyl Sulphone

This reaction was carried out according to procedure used for porphyrinate **10** and chloromethyl-phenyl sulphone (see above). Modifications: in the second portion 44 mg (0.39 mmol) of *t*-BuOK was added.

The products were isolated by column chromatography (eluent: $CHCl_3$/MeOH, 100:1) followed by purification on preparative TLC plates (eluent: $CHCl_3$/MeOH, 100:1) to afford:

a) [2,7,13-trinitro-3,8,12-tris{(toluene-4-sulphonyl)methyl}-5,10,15,20-tetraphenylporpyrinato]copper(II) (**20**); 29.7 mg (61%);

b) [2,7,13-trinitro-β,β-bis{(toluene-4-sulphonyl)methyl-5,10,15,20-tetraphenylporphyrinato]copper(II) (**21**, one of three possible isomers was formed); 10.3 mg (24%).

[2,7,13-Trinitro-3,8,12-tris{(toluene-4-sulphonyl)methyl}-5,10,15,20-tetraphenylporphyrinato]copper(II) (**20**): R_f=0.13 ($CHCl_3$/MeOH, 50:1). m.p. > 300ºC. UV-vis ($CHCl_3$); λ_{max} [nm] (log ε): 672.5 (4.06), 611.5 (3.98), 483 (4.92; Soret band), 339 (4.42). MS (ESI), *m/z* (% rel. int.): 1341 (10), 1340 (16), 1339 (23), 1338 (23), 1337 (26) [isotope $(M+Na)^+$]; 1318 (38), 1317 (64), 1316 (100), 1315 (81), 1314 (86) [isotope M^+ and $(M+H)^+$]; 1163 (10), 1162 (15), 1161 (23), 1160 (22), 1159 (26) [isotope $(M–SO_2Tol)^+$]; 875 (11), 874 (16), 873 (30), 872 (24), 871 (41). HR-MS (ESI): calcd for $C_{68}H_{49}N_7O_{12}S_3Cu$ (M^+) – 1314.1897; found – 1314.1899. The molecular formula was also confirmed by comparing the theoretical and experimental isotope pattern for the $(M+Na)^+$ ion ($C_{68}H_{49}N_7O_{12}S_3CuNa$) – it was found to be identical within the experimental error limits.

[2,7,13-Trinitro-β,β-bis{(toluene-4-sulphonyl)methyl}-5,10,15,20-tetraphenylporphyrinato]copper(II) (**21**, one of three possible isomers): R_f=0,38 ($CHCl_3$/MeOH, 50:1). m.p. > 300ºC. UV-vis ($CHCl_3$); λ_{max} [nm] (log ε): 650.5 (3.71), 602.5 (3.73), 472.5 (4.64; Soret band), 336.5 (4.11). MS (ESI), *m/z* (% rel. int.): 1151 (22), 1150 (38), 1149 (65), 1148 (92), 1147 (94), 1146 (100) [isotope M^+]. MS (ESI; after addition of AcONa), *m/z* (% rel. int.): 1173 (29), 1172 (52), 1171 (85), 1170 (72), 1169 (100) [isotope $(M+Na)^+$]. The molecular formula was confirmed by comparing the theoretical and experimental isotope pattern for the M^+ ion ($C_{60}H_{41}N_7O_{10}S_2Cu$) and $(M+Na)^+$ ion ($C_{60}H_{41}N_7O_{10}S_2CuNa$) – it was found to be identical within the experimental error limits.

Reaction of [2,7,13-Trinitro-5,10,15,20-tetraphenylporphyrinato] copper(II) (**18**) with Chloromethyl-Phenyl Sulphone

This reaction was carried out according to procedure used for porphyrinate **10** and chloromethyl-phenyl sulphone. Modifications: in the second portion 50 mg (0.45 mmol) of *t*-BuOK was added.

The product was isolated by column chromatography (eluent:

$CHCl_3$ → $CHCl_3$/MeOH, 100:1) followed by purification on preparative TLC plates (eluent: $CHCl_3$/MeOH, 100:1) to afford 35.8 mg of [2,7,13-trinitro-3,8,12-tris{(phenylsulphonyl)methyl}-5,10,15,20-tetraphenylporphyrinato]copper(II) (**22**); 76%.

[2,7,13-Trinitro-3,8,12-tris{(phenylsulphonyl)methyl}-5,10,15,20-tetraphenylporphyrinato]copper(II) (**22**): m.p. > 300ºC. UV-vis ($CHCl_3$); λ_{max} [nm] (log ε): 672.5 (4.02), 611.5 (3.96), 482.5 (4.89; Soret band), 347.5 (4.35). MS (ESI), *m/z* (% rel. int.): 1277 (22), 1276 (41), 1275 (69), 1274 (99), 1273 (89), 1272 (100) [isotope M^+ and $(M+H)^+$]. HR-MS (ESI): calcd for $C_{65}H_{43}N_7O_{12}S_3Cu$ (M^+) – 1272.1428; found – 1272.1415.

Reaction of [2,8,12-Trinitro-5,10,15,20-tetraphenylporphyrinato] copper(II) (**19**) with Chloromethyl–*para*-Tolyl Sulphone

This reaction was carried out according to procedure used for porphyrinate **10** and chloromethyl-phenyl sulphone. Modifications: (a) reaction scale: 0.058 mmol (47.4 mg of porphyrinate), (b) in the second portion 90 mg (0.80 mmol) of *t*-BuOK was added, (c) an additional portion of carbanion precursor was not added in this case.

The products were isolated by column chromatography (eluent: $CHCl_3$ → $CHCl_3$/MeOH, 250:1) followed by purification on preparative TLC plates (eluent: $CHCl_3$/MeOH, 100:1) to afford:

(a) [2,8,12-Trinitro-3,7,13-tris{(toluene-4-sulphonyl)methyl}-5,10,15,20-tetraphenylporphyrinato]copper(II) (**23**); 45.7 mg (60%);

(b) [2,8,12-Trinitro-β,β-bis{(toluene-4-sulphonyl)methyl}-5,10,15,20-tetraphenylporphyrinato]copper(II) (**24**; one of three possible isomers was formed); 22.8 mg (34%).

[2,8,12-Trinitro-3,7,13-tris{(toluene-4-sulphonyl)methyl}-5,10,15,20-tetraphenylporphyrinato]copper(II) (**23**): R_f=0,06 ($CHCl_3$/MeOH, 50:1). m.p.>300ºC. UV-vis ($CHCl_3$); λ_{max} [nm] (log ε): 669.5 (3.94), 612 (3.92), 491 (4.78; Soret band), 349.5 (4.29). MS (ESI), *m/z* (% rel. int.): 1342 (8), 1341 (24), 1340 (56), 1339 (100), 1338 (98), 1337 (96) [isotope $(M+Na)^+$]. HR-MS (ESI): calcd for $C_{68}H_{49}N_7O_{12}S_3CuNa$ [$(M+Na)^+$] – 1337.1795; found – 1337.1780.

[2,8,12-Trinitro-β,β-bis{(toluene-4-sulphonyl)methyl}-5,10,15,20-tetraphenylporphyrinato]copper(II) (**24**, one of three possible isomers): R_f = 0.22 ($CHCl_3$/MeOH, 50:1). m.p.>300ºC. UV-vis ($CHCl_3$); λ_{max} [nm] (log ε): 653 (3.41), 607 (3.41), 477 (4.29; Soret band), 338 (3.85). MS (ESI), *m/z* (% rel. int.): 1174 (6), 1173 (17), 1172 (43), 1171 (75), 1170 (69), 1169 (100) [isotope $(M+Na)^+$]. HR-MS (ESI): calcd for $C_{60}H_{41}N_7O_{10}S_2CuNa$ [$(M+Na)^+$] – 1169.1550; found – 1169.1541.

Reaction of [2,8,12-Trinitro-5,10,15,20-tetraphenylporphyrinato] copper(II) (**19**) with Chloromethyl-Phenyl Sulphone

This reaction was carried out according to procedure used for porphyrinate **19** and chloromethyl–*para*-tolyl sulphone (see above). Modifications: (a) reaction scale: 0.058 mmol (47.4 mg of porphyrinate), (b) the solution of substrates was dropped to a stirred *t*-BuOK (168 mg, 1.50 mmol) in DMSO (10 mL).

The product was isolated by column chromatography (eluent: $CHCl_3$/MeOH, 250:1) to afford [2,8,12-trinitro-3,7,13-tris{(phenylsulphonyl)methyl}-5,10,15,20-tetraphenylporphyrinato] copper(II) (**25**); 50.1 mg (68%).

[2,8,12-Trinitro-3,7,13-tris{(phenylsulphonyl)methyl}-5,10,15,20-tetraphenylporphyrinato]copper(II) (**25**): m.p. > 300ºC. UV-vis ($CHCl_3$); λ_{max} [nm] (log ε): 672 (3.80), 616 (3.77), 493 (4.68; Soret band), 353 (4.17). MS (ESI), *m/z* (% rel. int.): 1300 (8), 1299 (22), 1298 (52), 1297 (100), 1296 (94), 1295 (88) [isotope $(M+Na)^+$]. HR-MS (ESI): calcd for $C_{65}H_{43}N_7O_{12}S_3CuNa$ [$(M+Na)^+$] – 1295.1326; found – 1295.1310. The molecular formula was also confirmed by comparing the theoretical and experimental isotope pattern for the $(M+Na)^+$ ion ($C_{65}H_{43}N_7O_{12}S_3CuNa$) – it was found to be identical within the experimental error limits.

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