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SYNTHESIS OF PORPHYRIN–ACETYLENE AND PORPHYRIN–DIENE BUILDING BLOCKS FOR NEW DYADS PREPARATION

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Abstract – A new synthetic approach to porphyrin–acetylene and porphyrin–diene derivatives utilizing tetraphenylporphyrin (TPP) and two new reactions (vicarious nucleophilic substitution and metathesis) is described. 5-(4-Nitrophenyl)-10,15,20-triphenylporphyrin zinc complex reacts with $^{-}$CHXY type carbanions, affording the nucleophilic substitution of hydrogen products containing CH_2SO_2Tol, CH_2SO_2Ph, $CH_2SO_2NMe_2$, and CH_2CN groups, respectively. The products obtained when alkylated with alkyl halides, bearing an acetylenic function in the terminal position, resulted in the formation of TPP–acetylene building blocks. These systems were subjected to cross-enyne metathesis reaction with ethylene (with the use of efficient ruthenium catalysts) to give the porphyrin–diene dyads – the excellent substrates for further transformations.

INTRODUCTION

In the past decade, many dyads containing porphyrinyl component have been synthesized,[1] and some of these systems (*e.g.* porphyrin–fullerene dyads) have been studied as promising artificial photosynthetic models.[2] Also our research program was focused in part upon the utilization of the readily available tetraphenylporphyrin (by its selective derivatization) to prepare compounds of dual properties. Amongst related projects, the synthesis of porphyrin–fullerene dyads (containing $-CH_2-$ and $-(CH_2)_4-$ carbon chain linkages between two electronically labile parts of the target molecule) was undertaken.[3,4]

Herein, we would like to extend this methodology for synthesis of various porphyrin–acetylene and porphyrin–diene building blocks, bearing SO_2Tol, SO_2Ph, SO_2NMe_2, and CN substituents, and spacers of a length from $-(CH_2)-$ to $-(CH_2)_9-$.

RESULTS AND DISCUSSION

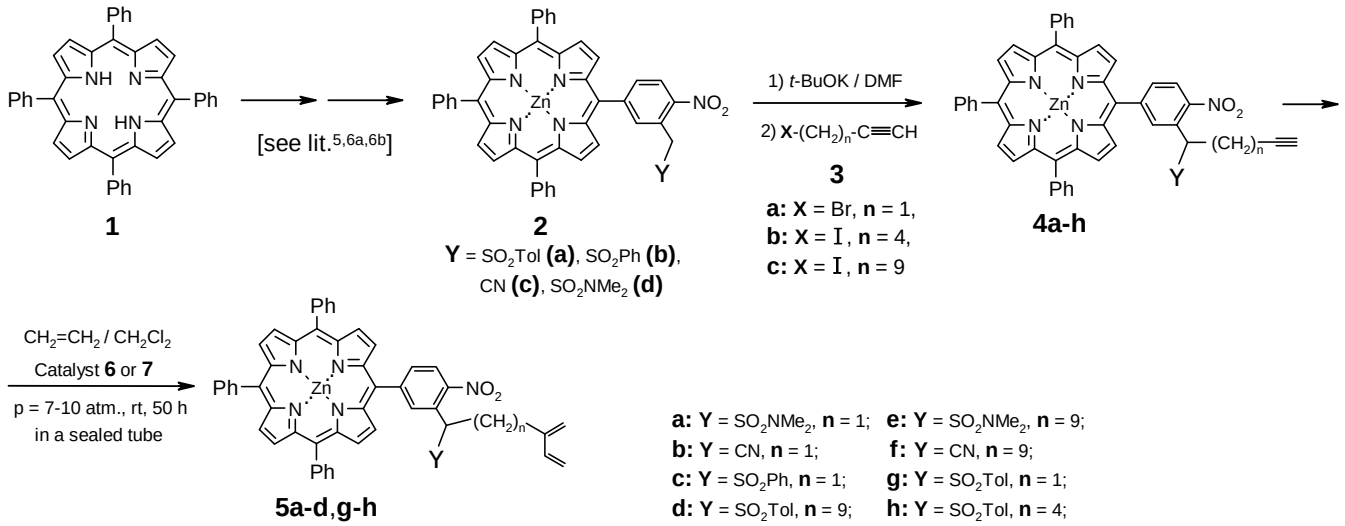
For our studies, TPP (**1**) was used as a starting material. Its selective mono-nitration in one of the phenyl rings gave 5-(4-nitrophenyl)-10,15,20-triphenylporphyrin.[5,6a,6b] We have already demonstrated that this

intermediate, after complexation with zinc or copper cations (with a yield usually >95%), readily enter the so-called vicarious nucleophilic substitution.[4,6]

This gives rise to an opportunity for the introduction of the next substituent (*e.g.* the carbon substituent, after reaction with the respective carbanion, to give compounds of type (**2**); Scheme 1). By this way we have synthesized porphyrin derivatives substituted in *meso*-nitroaryl ring with various groups, in high or satisfactory yield (-CH_2SO_2Ar, -$CH_2SO_2NMe_2$, -$CH_2SO_2Bu^t$, -CH_2CN, etc.; 50%-92%).[6a,6b] Some of them were used for further transformations herein.

These valuable intermediates (**2a-d**), bearing methylene hydrogen atoms of high acidity, when alkylated with alkyl halides of the type (**3**) (*t*-BuOK/DMF, 0°C), lead to the molecules with a terminal acetylenic unit in the carbon chain, tethered to the substituent at the nitrophenyl ring (compounds **4a-h**).

The yields of the above crucial step were satisfactory (35%-88%), except the alkylation with the use of long carbon chain halide (**3c**) (products **4e**, **4f**; 23% and 22% respectively). The acetylene derivatives obtained could be, as such, the valuable precursors for further transformations (*e.g.*, electrophilic addition to triple bond,[7] cycloaddition,[8] metathesis,[9] etc.), thus allowing the synthesis of a series of various dyads, bearing porphyrinyl parts.

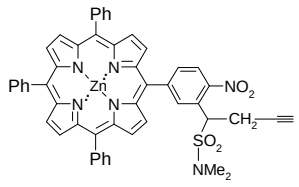
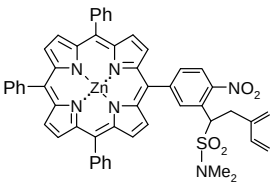
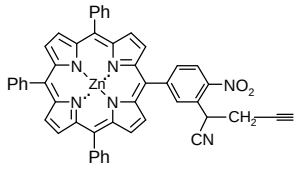
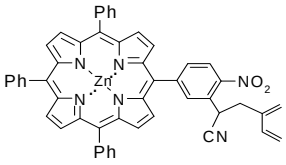
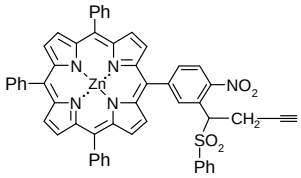
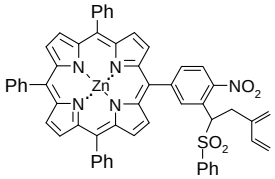
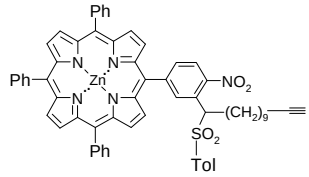
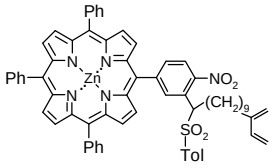
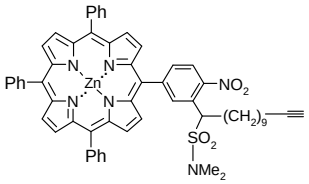
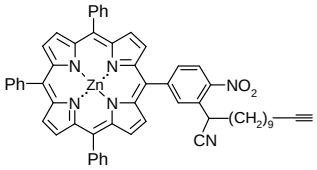
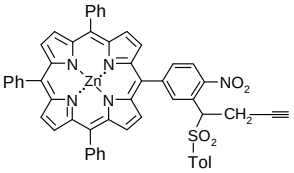
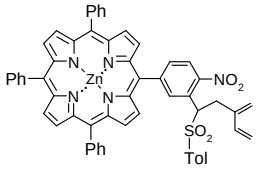
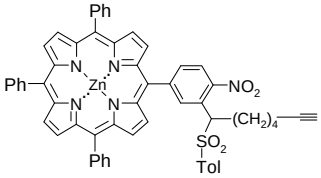
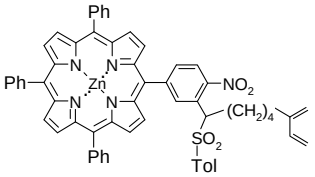


Scheme 1

In the next step of this research program the metathesis reaction caught our attention because of its unique ability to form C-C bonds, and the possibility to synthesise very attractive porphyrin–diene building blocks. In recent years, the applications of this approach have dramatically increased due to the availability of well-defined catalysts.[10]

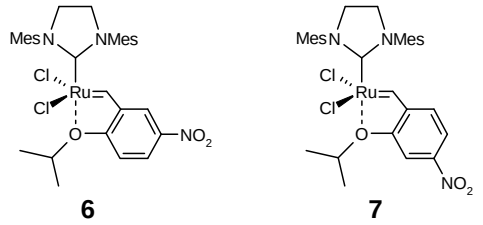
Thus, the key intermediates of type (**4**) were subjected to enyne intermolecular metathesis with ethylene to afford the dienes (**5**). In our previous paper the preparative protocol was proposed for this transformation (**4** → **5**), resulting in considerable improve of the yields.[4] We found that the application of second generation Hoveyda-type ruthenium catalysts[11] (recently developed in Grela's group[11c]), under higher pressure of ethylene (*ca.* 10 atm.), gave the best results.

Table 1. Products and the yields.

Acetylene Derivative		Yield [%]	Diene		Yield [%]	Catalyst
	**4a**	64		**5a**	67	**6**
	**4b**	35		**5b**	44	**6**
	**4c**	66		**5c**	85	**7**
	**4d**	37		**5d**	<5	**6**
	**4e**	23	No metathesis		–	**6**
	**4f**	22	No metathesis		–	**6**
	**4g**	50*)		**5g**	84*)	**6**
	**4h**	52*)		**5h**	86*)	**6**

*) data from the literature[4]

Herein, we used catalysts (**6** and **7**) (Figure 1). The metathesis was carried-out in a sealed tube in ethylene gas atmosphere (under pressure *ca*. 7-10 atm.), at room temperature for *ca*. 2 days, thus affording the porphyrin–diene building blocks (**5a-d,g,h**).



6 **7**

Figure 1

This reaction sequence allows the synthesis of the final dienes with shorter or longer spacers between chromophores (Scheme 1). The transformational yields were high or satisfactory; except the transformations of the acethylene derivatives into TPP–diene building blocks which bear long carbon chain linkages. In this case, despite repeated chromatographic separations, we were unable to isolate (or to detect) the desired products (from substrates (**4e**, **4f**) – no reaction; from compound (**4d**) – yield of *ca*. 5%). This could be due to instability of the final products. It is possible that the dyads produced, bearing diene unit at the ω-position of the long labile carbon chain, could enter spontaneously the [4+2] cycloaddition (inter- or intramolecular) with β,β-double bonds of pyrrole units,[12] thus causing the decomposition processes (many polar unidentified compounds were observed on TLC).

CONCLUSIONS

We presented herein a new approach to the synthesis of porphyrin–acetylene and porphyrin–diene building blocks utilizing tetraphenylporphyrin (TPP), new reactions, and new efficient metathesis catalysts. This method opens up the possibility for the preparation of such derivatives with variable distances between chromophores, depending on the type of the alkyl halides used. We believe they should give an opportunity for further transformations and the synthesis of very attractive systems (*e.g.* porphyrin–fullerene dyads).

EXPERIMENTAL

General. – ^{1}H NMR spectra were recorded with a Varian GEMINI-200 spectrometer operating at 200 MHz. Coupling constants *J* are expressed in hertz [Hz]. MS spectra were measured with an AMD 604 (AMD Intectra GmbH, Germany) spectrometer (electron impact method) and MARINER (ESI-TOF) PerSeptive Biosystems spectrometer (ESI method); *m/z* intensity values for peaks are given as % of relative intensity. UV-VIS spectra were measured with a Beckman DU-68 spectrophotometer. TLC analysis was performed on aluminium foil plates pre-coated with silica gel (60F 254, Merck). Silica gel, 230-400 mesh (Merck AG), was used for column chromatography. Molecular formulas of the compounds synthesised were confirmed by HR-MS (ESI) spectrum, or (for large molecular weight compounds) by comparison of the isotope molecular patterns (theoretical and experimental).

Porphyrin intermediates (**2a-d**) were obtained from TPP (**1**) according to the method previously developed in our laboratory.[6]

Alkylation of Porphyrins 2a-d. General Procedure. – To a solution of porphyrin (**2a-d**) (0.03 mmol) in anhydrous DMF (1.5 mL, under argon), *t*-BuOK (13 mg, 0.12 mmol) was added at 0°C, and the mixture

was stirred for 10 min. Then, propargyl bromide (**3a**) or 11-iodo-1-undecyn (**3c**) (0.24 mmol) in DMF (0.5 mL) was added dropwise *via* syringe (over a period of *ca* 5 min), and the reaction was continued at 0°C for 1.5 h. Then, the subsequent portions of *t*-BuOK (10 mg, 0.089 mmol) and alkyl halide (0.18 mmol; in 0.5 mL of DMF) were added. After an additional 1.5 h of stirring at this temperature, the mixture was poured onto water containing ice (30 mL).*) The precipitate was filtered, washed with water (3 × 30 mL), and then dissolved in $CHCl_3$ (40 mL). After drying over $MgSO_4$ and evaporating the solvent, the desired products were isolated by column chromatography (eluent: $CHCl_3$/*n*-hexane, 4:1) to give: **4a** – 17 mg (64%); **4b** – 8.5 mg (35%); **4c** – 18 mg (66%); **4d** – 11.5 mg (37%); **4e** – 7 mg (23%); **4f** – 6 mg (22%).

*) In the case of reactions with 11-iodo-1-undecyn after 1.5 h, the subsequent portions of *t*-BuOK (7 mg, 0.063 mmol) and alkyl halide (42 mg, 0.15 mmol; in 0.5 mL of DMF) were added and the reaction was continued with stirring for the further 1 h.

(4a): – mp >300°C. – ^{1}H NMR ($CDCl_3$, 200 MHz): 9.09 (d, J = 4.7 Hz, 1H, H$^\beta$-pyrrole), 9.05-8.84 (m, 7H, H$^\beta$-pyrrole), 8.71 (d, J = 1.6 Hz, 1H, H-2 of H-Ar(NO_2)), 8.34 (part of AB coupled with another proton, J = 8.1, 1.6 Hz, 1H, H-6 of H-Ar(NO_2)), 8.28 (part of AB, J = 8.1 Hz, 1H, H-5 of H-Ar(NO_2)), 8.26-8.17 (m, 6H, H-Ph), 7.82-7.70 (m, 9H, H-Ph), 6.07 (apparent t, J = 7.7 Hz, 1H, C<u>H</u>(SO_2NMe_2)), 3.27 (dd, J = 7.7, 2.6 Hz, 2H, CH_2), 2.92 (s, 6H, N(CH_3)$_2$), 2.12 (t, J = 2.6 Hz, 1H, C≡CH). – UV-VIS ($CHCl_3$), λ_{max} (log ε): 587 (3.79), 548.5 (4.50), 510.5 (3.71), 419.5 nm (5.72, Soret). – MS (EI), *m/z* (% rel. int.): 886 (0.1), 885 (0.1), 884 (0.1), 883 (0.2), 882 (0.1), 881 (0.1), and 880 (0.3) [isotopic $M^{+\cdot}$]; MS (ESI), *m/z* (% rel. int.): 886 (23), 885 (39), 884 (60), 883 (61), 882 (85), 881 (68), and 880 (100) [isotopic M^+]; HR-MS (ESI) calcd for $C_{50}H_{36}N_6O_4SZn$ (M^+) – 880.1810, found – 880.1817. The molecular formula was also confirmed by comparing the theoretical and experimental isotope patterns for the M^+ ion ($C_{50}H_{36}N_6O_4SZn$) – found to be identical within the experimental error limits.

(4b): – mp >300°C. – ^{1}H NMR ($CDCl_3$, 200 MHz): 9.10-8.77 (m, 8H, H$^\beta$-pyrrole), 8.56-8.42 (m, 3H, H-Ar(NO_2)), 8.35-8.15 (m, 6H, H-Ph), 7.85-7.66 (m, 9H, H-Ph), 5.42-5.30 (m, 1H, C<u>H</u>(CN)), 3.27-3.18 (m, 2H, CH_2), 2.02 (br s, 1H, C≡CH). – UV-VIS ($CHCl_3$), λ_{max} (log ε): 587.5 (3.36), 548.5 (3.90), 505 (3.48), 421 nm (4.91, Soret). – MS (EI), *m/z* (% rel. int.): 798 (0.6, $M^{+\cdot}$), 771 (2), 770 (2), 769 (2), 768 (3), 767 (3), 766 (3), 746 (2), 745 (3), 744 (2), 743 (4), 742 (5), 741 (6), 740 (2), 739 (0.6), 694 (0.9), 693 (2), 692 (2), 691 (2), 690 (0.8), 689 (0.7), 688 (1), 668 (0.6), 667 (1), 666 (1), 665 (2), 664 (2), 663 (2), 662 (0.9), 603 (0.5), 602 (1), 601 (1), 600 (2), 599 (2), 598 (1), 597 (1), 596 (2), 522 (1.5), 521 (0.8), 400 (1.5), 399 (4), 398 (8), 397 (6.5), 77 (32), 55 (100), 44 (80, CO_2^+); MS (ESI), *m/z* (% rel. int.): 804 (5), 803 (7), 802 (8), 801 (10), 800 (12), 799 (11), and 798 (11) [isotopic M^+ and $(M+H)^+$]; *m/z* (M^+) = 798.2 (calcd – 798.2).

(4c): – mp >300°C. – ^{1}H NMR ($CDCl_3$, 200 MHz): 9.10 (d, J = 4.8 Hz, 1H, H$^\beta$-pyrrole), 9.06-8.91 (m, 6H, H$^\beta$-pyrrole), 8.88 (d, J = 4.8 Hz, 1H, H$^\beta$-pyrrole), 8.71 (apparent s, 1H, H-2 of H-Ar(NO_2)), 8.34 (part of AB coupled with another proton, J = 8.6, 1.3 Hz, 1H, H-6 of H-Ar(NO_2)), 8.29 (part of AB, J = 8.6 Hz, 1H,

H-5 of H-Ar(NO_2)), 8.27-8.18 (m, 6H, H-Ph), 7.92-7.53 (m, 14H, 9H of H-Ph and 5H of H-SO_2Ph), 6.08 (apparent t, J = 7.9 Hz, 1H, C<u>H</u>(SO_2Ph)), 3.28 (dd, J = 7.9, 2.3 Hz, 2H, CH_2), 2.10 (t, J = 2.3 Hz, 1H, C≡CH). – UV-VIS ($CHCl_3$), λ_{max} (log ε): 590 (3.70), 548 (4.38), 514.5 (3.64), 419.5 (5.62, Soret), 340.5 (4.14), 318 nm (4.27). – MS (ESI), *m/z* (% rel. int.): 919 (21), 918 (42), 917 (68), 916 (74), 915 (95), 914 (76), and 913 (100) [isotopic M^+]; HR-MS (ESI) calcd for $C_{54}H_{35}N_5O_4SZn$ (M^+) – 913.1701, found – 913.1677. The molecular formula was also confirmed by comparing the theoretical and experimental isotope patterns for the M^+ ion ($C_{54}H_{35}N_5O_4SZn$) – found to be identical within the experimental error limits.

(4d): – mp >300°C. – ^{1}H NMR ($CDCl_3$, 200 MHz): 9.05 (d, J = 4.9 Hz, 1H, H^β-pyrrole), 9.02-8.79 (m, 6H, H^β-pyrrole), 8.75 (d, J = 4.8 Hz, 1H, H^β-pyrrole), 8.60-8.43 (m, 3H, H-Ar(NO_2)), 8.30-8.15 (m, 6H, H-Ph), 7.85-7.68 (m, 11H, 9H of H-Ph and 2H of H-Tol), *ca*. 7.40 (part of AA'XX', 2H, H-Tol), 5.53-5.34 (m, 1H, C<u>H</u>(SO_2Tol)), 3.21-3.08 (m, 2H, CH_2), 2.50-2.41 (m, 2H, CH_2), 2.35 (s, 3H, CH_3), 2.10-1.48 (m, 15H, C≡CH and 7×CH_2). – UV-VIS ($CHCl_3$), λ_{max} (log ε): 586.5 (3.02), 547.5 (3.61), 513.5 (3.03), 420 nm (4.90, Soret). – MS (ESI), *m/z* (% rel. int.): 1019 (2), 1018 (5), 1017 (7), 1016 (8), 1015 (9), and 1014 (9) [isotopic M – C≡CH], 1013 (10), 974 (3), 973 (3), 972 (4), 971 (4), 970 (4), 969 (2), 968 (2), 892 (20), 891 (34), 890 (50), 889 (79), 888 (73), 887 (100), 886 (44), 885 (47); HR-MS (ESI) calcd for $C_{61}H_{52}N_5O_4SZn$ (M−C≡CH) – 1014.3031, found – 1014.2601; calcd for $C_{56}H_{47}N_5O_2Zn$ [(M+H)−SO_2Tol] – 885.3021, found – 885.2901.

(4e): main product in the mixture (*ca*. 95% purity); for contaminated product UV-VIS and MS spectra were recorded; – UV-VIS ($CHCl_3$), λ_{max}: 589, 549, 506.5, 418.5 (Soret), 310 nm. – MS (ESI), *m/z* (% rel. int.): the molecular ion was not detected, characteristic fragmentation ions [M−NO_2−$N(CH_3)_2$−O] were detected: 893 (7), 892 (17), 891 (26), 890 (44), 889 (45), 888 (64), 887 (39), and 886 (43) [isotopic ions].

(4f): main product in the mixture (*ca*. 95% purity); for contaminated product UV-VIS and MS spectra were recorded; – UV-VIS ($CHCl_3$), λ_{max}: 589.5, 549, 507, 419.5 nm (Soret). – MS (ESI), *m/z* (% rel. int.): the molecular ion was not detected, characteristic fragmentation ions [M−OH−CN] were detected: 875 (22), 874 (32), 873 (61), 872 (60), 871 (94), 870 (73), 869 (100), 868 (39), and 867 (56) [isotopic ions].

Data for compound (**4g** and **4h**) – see lit.[4]

Metathesis transformation. – A pressure tube (50 mL) was thoroughly flushed with argon and charged with a solution of an alkyne derivative (**4a-4d**, 0.008 mmol) and the catalyst (**6** or **7** for **4c**; *ca* 20% mol) in anhydrous CH_2Cl_2 (2 mL). The tube was immersed in liquid nitrogen (*ca*. -190°C) and gaseous ethylene was delivered to the tube through rubber septa. After an accumulation of ethylene, the tube was sealed and the reaction mixture was allowed to reach room temperature. The mixture was stirred under the ethylene gas atmosphere (7-10 atm.) for approximately 50 h. Then it was recooled in liquid nitrogen and the tube

was opened. The mixture was allowed to reach room temperature under stream of argon. The residue was concentrated under reduced pressure and purified by column chromatography (eluent: $CHCl_3$); yields: **5a**, 4.9 mg (67%) – from **4a**; **5b**, 2.9 mg (44%) – from **4b**; **5c**, 6.4 mg (85%) – from **4c**; **5d**, 0.4 mg (<5%) – from **4d**.

(5a): – mp >300°C. – ^{1}H NMR ($CDCl_3$, 200 MHz): 9.01 (d, *J* = 5.0 Hz, 1H, H^{β}-pyrrole), 8.96 (s, 4H, H^{β}-pyrrole), 8.88-8.68 (m, 4H, 3H of H^{β}-pyrrole and H-2 of H-Ar(NO_2)), 8.45-8.00 (m, 8H, H-5 and H-6 of H-Ar(NO_2) and 6H of H-Ph), 7.87-7.68 (m, 9H, H-Ph), 6.41 (dd, *J* = 17.3, 11.0 Hz, 1H, H-vinyl), 5.96-5.85 (m, 1H, C<u>H</u>(SO_2NMe_2)), 5.37-5.05 (m, 4H, 2×CH_2-vinyl), 4.58-4.27 (m, 2H, CH_2), 2.94 (s, 6H, $N(CH_3)_2$). – UV-VIS ($CHCl_3$), λ_{max} (log ε): 585.5 (3.41), 547.5 (3.96), 511 (3.52), 419.5 nm (5.17, Soret). – MS (ESI), *m/z* (% rel. int.): 918 (3.5), 917 (6.5), 916 (7), 915 (11), 914 (11), 913 (18), 912 (8), 911 (9.5), 910 (7), 909 (8), and 908 (6) [isotopic M^+ and $(M+H)^+$]; HR-MS (ESI) calcd for $C_{52}H_{40}N_6O_4SZn$ (M^+) – 908.2123, found – 908.2105.

(5b): – mp >300°C. – ^{1}H NMR ($CDCl_3$, 200 MHz): 8.91-8.77 (m, 8H, H^{β}-pyrrole), 8.29 (d, *J* = 2.8 Hz, 1H, H-2 of H-Ar(NO_2)), 8.20-8.11 (m, 7H, H-5 of H-Ar(NO_2) and 6H of H-Ph), 8.05 (dd, *J* = 8.8, 2.8 Hz, 1H, H-6 of H-Ar(NO_2)), 7.74-7.62 (m, 9H, H-Ph), 5.37-5.00 (m, 6H, C<u>H</u>(CN) and 5×H-vinyl), 4.17-3.96 (m, 2H, CH_2). – UV-VIS ($CHCl_3$), λ_{max} (log ε): 585.5 (3.19), 549.5 (3.64), 508 (3.29), 420.5 nm (4.83, Soret). – MS (ESI), *m/z* (% rel. int.): 839 (7), 838 (7), 837 (10), 836 (14), 835 (18), 834 (16), 833 (20), 832 (20), 831 (22), 830 (13), 829 (12), 828 (14), 827 (15), and 826 (16) [isotopic M^+ and $(M+H)^+$]; *m/z* (M^+) = 826.2 (calcd – 826.2).

(5c): – mp >300°C. – ^{1}H NMR ($CDCl_3$, 200 MHz): 9.09 (d, *J* = 4.7 Hz, 1H, H^{β}-pyrrole), 9.02-8.93 (m, 5H, H^{β}-pyrrole), 8.91 (d, *J* = 4.7 Hz, 1H, H^{β}-pyrrole), 8.77 (d, *J* = 1.5 Hz, 1H, H-2 of H-Ar(NO_2)), 8.72 (d, *J* = 4.7 Hz, 1H, H^{β}-pyrrole), 8.31-8.17 (m, 7H, H-6 of H-Ar(NO_2) and 6H of H-Ph), 8.15 (part of AB, *J* = 8.2 Hz, 1H, H-5 of H-Ar(NO_2)), 7.95-7.52 (m, 14H, H-Ph), 6.36 (dd, *J* = 17.7, 10.7 Hz, 1H, H-vinyl), 6.08 (dd, *J* = 11.6, 3.4 Hz, 1H, C<u>H</u>(SO_2Ph)), 5.30-5.00 (m, 4H, 2×CH_2-vinyl), 4.35-4.02 (m, 2H, CH_2). – UV-VIS ($CHCl_3$), λ_{max} (log ε): 588 (3.72), 548 (4.31), 507 (3.77), 419.5 (5.52, Soret), 340.5 nm (4.35). – MS (ESI), *m/z* (% rel. int.): 948 (6), 947 (9), 946 (14), 945 (15), 944 (18), 943 (18), 942 (21), and 941 (10) [isotopic M^+ and $(M+H)^+$]; *m/z* (M^+) = 941.2 (calcd – 941.2).

(5d): the product was obtained in a small amounts (<5%); it was analyzed by UV-VIS and MS spectra; – UV-VIS ($CHCl_3$), λ_{max} (log ε): 585.5, 548, 509.5, 420 nm (Soret). – MS (ESI), *m/z* (% rel. int.): 924 (5), 923 (5), 922 (9), 921 (7), 920 (11); 893 (12), 892 (32), 891 (58), 890 (65), 889 (93), and 888 (89) [isotopic $M-(CH_2)_9$-$C(CH_2)$-$CH=CH_2$]; 887 (100); *m/z* ($C_{52}H_{34}N_5O_4SZn$) = 888.3 (calcd – 888.2).

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