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Synthesis and Estimation of Radical Scavenging Activity of Tetra(*meso*-aryl)porphyrins Containing 2,6-Dimethoxyphenol Unit

T. K. Rocheva[a]*, L. I. Mazaletskaya[b], N. I. Sheludchenko[b], and D. V. Belykh[a]

[a] *Institute of Chemistry, Komi Scientific Center, Ural Branch, Russian Academy of Sciences, ul. Pervomaiskaya 48, Syktyvkar, 167000 Russia*
**e-mail: tatyanrocheva@yandex.ru*

[b] *Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, Moscow, Russia*

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Abstract—Tetra(*meso*-aryl)porphyrins containing 2,6-dimethoxyphenol unit distant from the macrocycle and adjacent to it have been prepared. Radical scavenging activity of the obtained compounds has been estimated in the model reaction of ethylbenzene oxidation initiated by azobisisobutyronitrile. It has been shown that the phenol hydroxy group ability to inhibit ethylbenzene oxidation depends on the environment of phenol group.

Keywords: tetra(*meso*-aryl)porphyrins, substituted phenols, radical scavenging activity, stoichiometric inhibition coefficients, inhibited oxidation of ethylbenzene
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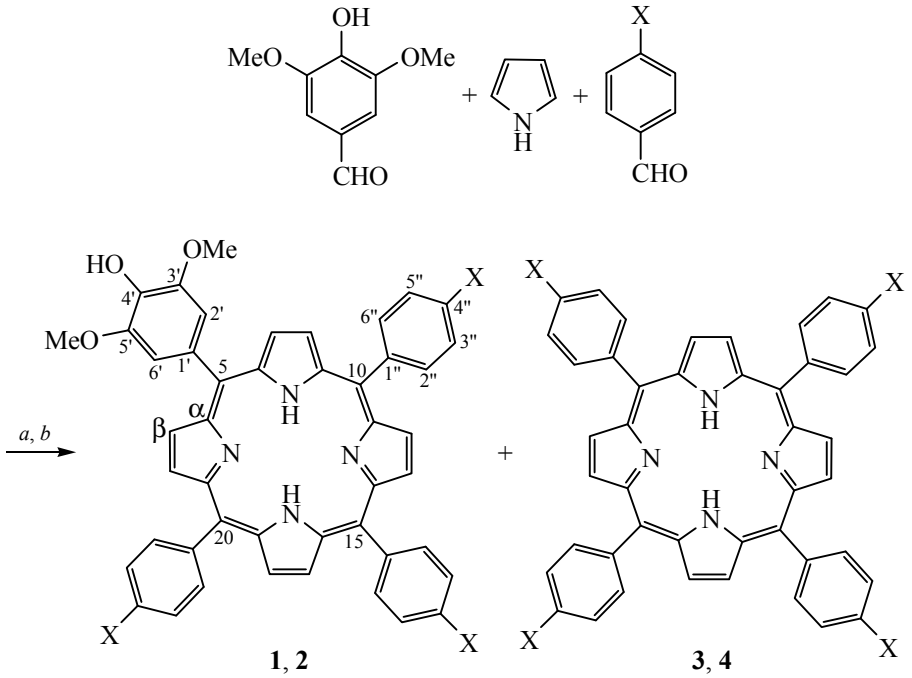
Free radical oxidation as a controlled process and indispensable part of living organisms functioning [1–6] includes many reactions involving different radicals and so-called reactive oxygen species. Free radicals play an important part in normal cell metabolism, being involved in oxidative phosphorylation, biosynthesis of prostaglandins and nucleic acids, regulation of lipid metabolism, and mythos processes. The formation of free radicals in excessive concentrations results in disorganization of all cellular structures, disorder of their functional activity, and cell death [7, 8]. In living organisms, complex antioxidant system exists which protects from radical damage; it includes enzymes (catalase, glutathione peroxidase, and superoxide dismutase), chelators for transition metals (albumin, ferritin, and ceruloplasmin), melatonin, amino acids, glutathione, peptides, certain vitamins and hormones [2, 9–12]. Disorders in antioxidant system may be compensated by the introduction of exogenic antioxidants [1].

One of the interesting modern directions is synthesis of hybrid antioxidants – molecules which exhibit antioxidant activity and are at the same time capable of targeted delivery and structural interactions with the biosystem [2], or molecules containing several reaction sites which can inhibit oxidation processes via diverse ways and exhibit intramolecular synergic effect [1, 13, 14]. Tetra(*meso*-aryl)porphyrins which contain substituents enhancing the radical scavenging activity (RSA) form a prospective class of such compounds [15–22]. Sub-stituted phenols are widely used antioxidants; their efficiency increases with the increase in the number of electron-donor substitutes in *ortho*- or *para*-positions with respect to OH-group.

We have earlier obtained a series of tetra(*meso*-aryl)porphyrins containing a phenol hydroxy group at one of aromatic substitutes and analogous compounds containing a methoxy group [15]. Their investigation has shown that compounds containing a phenol hydroxy group in *para*-position with respect to the macrocycle exhibit high RSA. The presence of 2,6-dimethoxyphenol unit in a hybrid macromolecule provides significant RSA; the +*M*-effect of two methoxy groups increases the activity of phenol hydroxy group despite its involvement in intramolecular hydrogen bond [15]. Hence, the investigation of the influence of the porphyrin part structure of the hybrid molecule on the RSA is important.

Scheme 1.



X = OCH_3 (**1**, **3**), H (**2**, **4**).

a, EtCOOH, reflux, 1 h; *b*, air oxidation, 5 days.

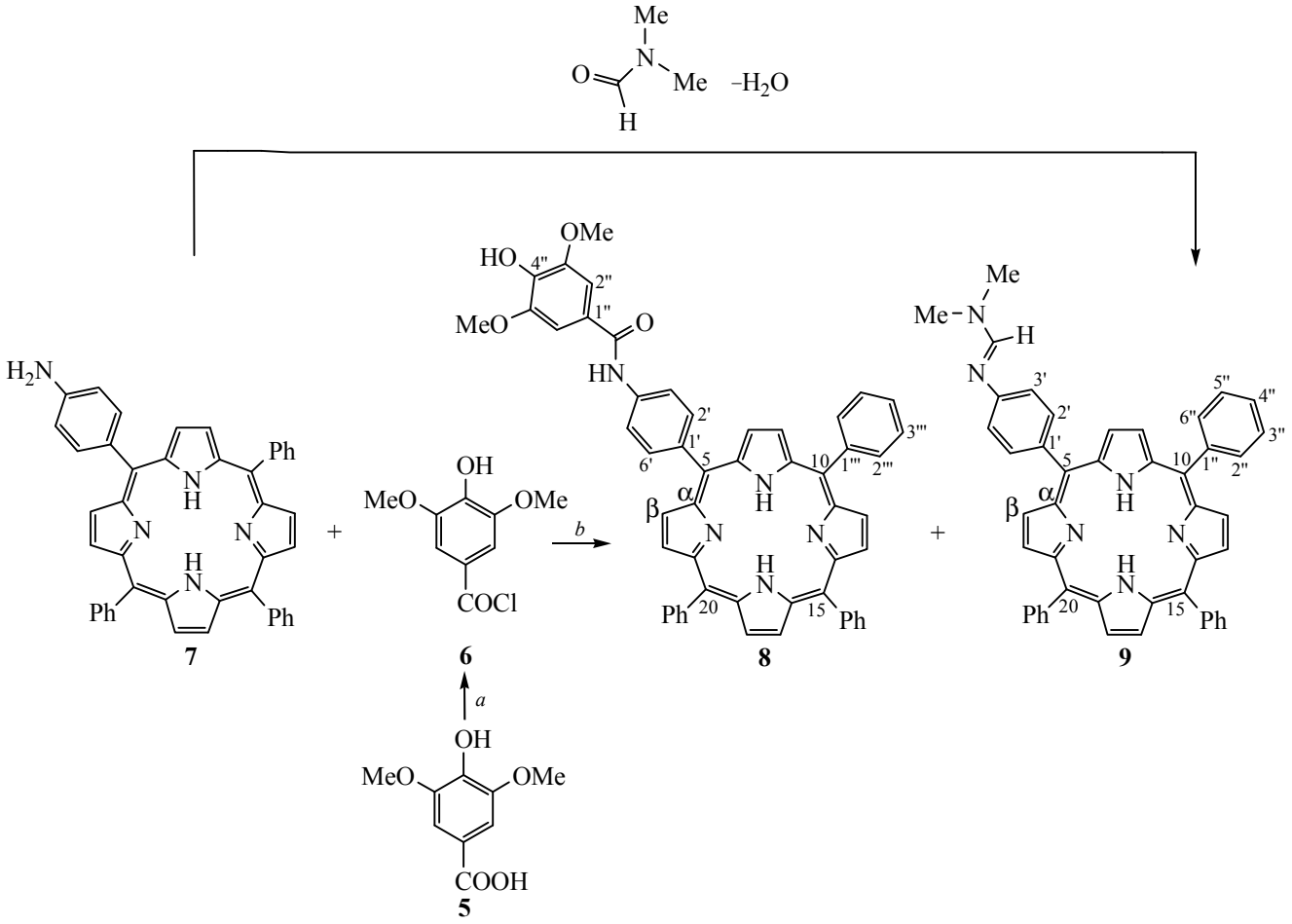
Herein we report the synthesis of tetra(*meso*-aryl) porphyrins with a 2,6-dimethoxyphenol unit directly bonded with porphyrin macrocycle and connected to it via a spacer; RSA of the prepared compounds has been estimated.

Asymmetrically substituted porphyrins **1** and **2** were synthesized via mixed-aldehyde–tetrapyrrole condensation of 4-hydroxy-3,5-dimethoxybenzaldehyde with 4-methoxybenzaldehyde (compound **1**) and benzaldehyde (compound **2**) during refluxing in propionic acid followed by oxidation with air (Scheme 1). Symmetrically substituted tetra(*meso*-aryl)porphyrins **3** and **4** were isolated as well as target products **1** and **2**.

Compound **8** containing a phenol antioxidant moiety distant from the macrocycle was prepared via the reaction of 5-(4'-aminophenyl)-10,15,20-triphenylporphin **7** with 4-hydroxy-3,5-dimethoxybenzoyl chloride **6** (prepared via the reaction between thionyl chloride and acid **5**) (Scheme 2). To optimize the conditions of the synthesis of compound **8**, we varied the molar ratio of compounds **6** and **7**. The use of threefold excess of the acylation agent **6** was found optimal. The yield of the acylation product **8** was 43% at the starting porphyrin **7** conversion 73%. Compound **9** was obtained as a side product. According to data from [23, 24], analogous product is formed in the reaction of DMF, acyl chlorides (acting as a dehydrating agent), and aromatic amines.

The structure of porphyrins **1**, **2**, **8**, and **9** was confirmed by means of IR, electronic, and NMR spectroscopy as well as mass spectrometry. The mass spectra of the prepared compounds contained peaks with *m/z* corresponding to the protonated molecular ions $[M + H]^+$. The Soret band and the absorption band characteristic of tetra-*meso*-substituted porphyrin chromophore were observed in the electron absorption spectra. The ^1H NMR spectra of compounds **1**, **2**, **8** and **9** contained proton signals of the porphyrin macrocycle (H^β-pyrrole and transannular NH-protons) and of the aromatic substitutes. The ^1H NMR spectrum of compound **9** contained the signals of methyl groups (δ_H 3.25 ppm) and of the proton at carbon atom of imine group (δ_H 7.99 ppm) of the formamide unit. The ^{13}C NMR spectrum contained carbon signals of syringic acid unit methoxy groups at δ_C 55.61, 56.61, and 56.74 ppm for porphyrins **1**, **2**, and **8**, respectively. The IR spectra of porphyrins **1**, **2**, and **8** contained the

Scheme 2.



a, CH_2Cl_2, $SOCl_2$, reflux, 1 h; *b*, CH_2Cl_2, DMF, reflux, 1 h.

absorbance bands corresponding to the stretching of phenol O–H bond as well as of the porphyrin macrocycle N–H bond.

The inhibiting activity of phenol-substituted porphyrins was investigated using a model reaction of oxidation of ethylbenzene initiated by azobisisobutyronitrile. The initial rate of oxygen absorption (w) in the presence of an antioxidant was determined from the kinetic curves. The stoichiometric inhibition coefficient (f) was determined from the induction period value (τ) using Eq. (1):

$$f = \tau \cdot w_i / c_0, \quad (1)$$

where w_i is the initiation rate, c_0 is the antioxidant concentration.

The rate constants of the reaction of antioxidant with peroxy radicals (k_{inh}) was determined by plotting the kinetic data in coordinates of Eq. (2):

$$w_0/w - w/w_0 = fk_{inh} \cdot c_0 / k_r^{0.5} \cdot w_i^{0.5}, \quad (2)$$

where w_0 and w are the rate constants in the absence and in the presence of antioxidant addition, respectively; k_r is the rate constant of bimolecular peroxy radicals recombination.

According to data listed in the table, RSA (f and k_{inh}) of the studied compounds depended on the substitution of the porphyrin cycle and phenol unit. Compound **1** containing additional methoxy substituents at the phenyl groups, in contrast to compound **2**, showed the higher rate constant of the reaction with free radicals. The fk_{inh} values for compounds **1** and **2** differed by 1.2 times at equal $f = 2$ values.

Similar increase in the k_{inh} constant caused by the introduction of additional alkoxy groups at the phenyl moiety has been previously observed in our studies of porphyrin derivatives containing phenol unit with the

Stoichiometric inhibition coefficients (*f*) and inhibition parameters (fk_{inh}) at 333 K

Inhibitor	*f*	$fk_{inh}\times10^{-4}$, L mol^{-1} s^{-1}
1	2.0	9.4
2	2.0	7.7
8	1.6	2.6

OH-group in *meta*-position with respect to porphyrin cycle, other substituents being absent [15].

Introduction of an electron acceptor group at the *p*-position of the phenol unit (compound **8**) resulted in the increase in the fk_{inh} parameter by about 3 times compared with compound **2** and by 3.6 times compared with compound **1**. At the same time, the decrease in the stoichiometric coefficient to $f = 1.6$ was observed.

In summary, tetra(*meso*-aryl)porphyrins containing 2,6-dimethoxyphenol unit distant from the macrocycle (compound **8**) and directly bonded to it (compounds **1** and **2**) were prepared, and their RSA was determined using a model reaction of ethylbenzene oxidation initiated by azobisisobutyronitrile at 333 K in air. The prepared porphyrins exhibited RSA depending on the substitution at the porphyrin macrocycle and phenol unit. Introduction of methoxy groups at the phenyl substituents of porphyrin accelerated its reaction with free radicals; the presence of electron acceptor group in the *para*-position of the phenol unit gave the opposite effect. In the latter case, the stoichiometric inhibition coefficient was reduced.

EXPERIMENTAL

The IR spectra were recorded using an IR Prestige 21 FTIR spectrometer in KBr pellets. The electronic absorption spectra were registered using a Shimadzu UV-1700 spectrometer in 10 mm quartz cells with chloroform or dichloromethane as referrence. The ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance II spectrometer (300 and 75 MHz) in $CDCl_3$. Mass spectra (ESI) were registered using a Thermo Finnigan LCQ Fleet device. The reaction course was monitored by thin layer chromatography on Sorbfil plates. Aluminum oxide (40/200 μm, "pure" grade) was used for column chromatography.

RSA was estimated in a model reaction of the ethylbenzene initiated oxidation at 333 K in an air atmosphere. Dinitrile of azoisobutyric acid was used as the initiator of free radicals, the initiation rate w_i was 5×10^{-8} mol L^{-1} s^{-1}. Ethylbenzene with a dissolved antioxidant was pre-thermostated. After that an initiator additive was added. The oxygen absorption kinetics was measured with a volumetric unit .

5-(4'-Hydroxy-3',5'-dimethoxyphenyl)-10,15,20-tri(4''-methoxyphenyl)porphin (1). A solution of 4-hydroxy-3,5-dimethoxybenzaldehyde (0.20 g, 1.10 mmol), 4-methoxybenzaldehyde (0.79 mL, 6.50 mmol), and pyrrole (0.52 mL, 7.50 mmol) in 20 mL of propionic acid was added to 15 mL of boiling propionic acid. The reaction mixture was refluxed for 0.5 h, kept at room temperature for 5 days in air, and diluted with chloroform (50 mL). Propionic acid and other water-soluble impurities were washed out with water to neutral reaction of the washings. The solution was dried over anhydrous sodium sulfate; the solvent was distilled off under reduced pressure. The obtained mixture of porphyrins **1** and **3** was separated using column chromatography on alumina. Yield 0.017 g (2%), purple crystal powder, R_f 0.76 (eluent—chloroform). IR spectrum (KBr), ν, cm^{-1}: 3537 (OH), 3318 (NH), 2837 (OCH_3), 2933, 1607 (C=C), 1508, 1468, 1350, 1213, 1111, 972, 802, 735, 700. ^{1}H NMR spectrum ($CDCl_3$), δ_H, ppm: –2.71 br.s (2H, NH), 4.05 s (6H, 5-ArOCH_3), 4.14 s (9H, 10,15,20-ArOCH_3), 5.91 s (1H, 5-ArOH), 7.33 d (6H, 10,15,20-Ar$H^{3'',5''}$, J_{HH} = 8.2 Hz), 7.52 s (2H, 5-Ar$H^{2',6'}$), 8.16 d (6H, 10,15,20-Ar$H^{2'',6''}$, J_{HH} = 8.3 Hz), 8.91 br.s (6H, $H^{2,8,12,13,17,18}$), 8.96 d (2H, $H^{3,7}$, J_{HH} = 4.6 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 55.61 (10,15,20-ArOCH_3), 56.60 (5-ArOCH_3), 112.24 (10,15,20-Ar$C^{3'',5''}$), 112.42 (5-Ar$C^{2',6'}$), 119.73, 119.84, 119.96 ($C^{5,10,15,20}$), 129.89–131.75 ($C^{\alpha,\beta}$), 133.48 (5-Ar$C^{3',5'}$), 134.61 (10,15,20-Ar$C^{2'',6''}$,-Ar$C^{4'}$), 135.56 (10,15,20-Ar$C^{4''}$), 145.36 (5-Ar$C^{1'}$), 159.46 (10,15,20-Ar$C^{1''}$). EAS (CH_2Cl_2), λ_{max}, nm (*I*, %): 649.5(1), 593.0(1), 555.0(2), 517.5(3), 422.5(100). Mass spectrum (ESI), *m*/*z*: 781.4 $[M + H]^+$ (calculated for $C_{49}H_{41}N_4O_6$: 781.3).

5-(4'-Hydroxy-3',5'-dimethoxyphenyl)-10,15,20-triphenylporphin (2) was prepared as described in [15]. Purple crystal powder, R_f 0.33 (eluent—tetrachloromethane–acetone, 10 : 1).

5,10,15,20-Tetra(*meso*-methoxyphenyl)porphin (3). Yield 0.035 g (3%), purple crystal powder, R_f 0.32 (eluent—tetrachloromethane–acetone, 100 : 1). Spectral characteristics were identical to those reported in [25].

5-(4'-Aminophenyl)-10,15,20-triphenylporphin (7) was prepared as described in [26]. Purple crystal powder, R_f 0.53 (eluent—tetrachloromethane–acetone, 5 : 1).

Acylation of porphyrin 7. A mixture of 4-hydroxy-3,5-dimethoxybenzoic acid (0.03 g, 0.15 mmol) and thionyl chloride (0.04 mL, 0.61 mmol) in dichloromethane was refluxed for 1 h. The solvent and volatile components were removed under reduced pressure. Dichloromethane (7 mL), dimethylformamide (0.1 mL), and a solution of porphyrin (0.03 g, 0.05 mmol) in dichloromethane (20 mL) were added to the obtained acyl chloride. The reaction mixture was refluxed for 1 h and then cooled down. Dilute hydrochloric acid (1 : 10) was added. The mixture was washed with water to neutral reaction of the washings. The obtained solution was dried over anhydrous sodium sulfate; the solvent was removed under reduced pressure. The reaction products were separated using column chromatography on alumina (eluent—tetrachloromethane, chloroform, chloroform–ethanol, 10 : 1). Porphyrins **7** (0.008 g, conversion 73%), **8** (0.012 g, 43%), and **9** (0.010 g, 42%) were isolated.

5-[4'-(*N*-4''-Hydroxy-3'',5''-dimethoxy)benzoylamino]phenyl-10,15,20-triphenylporphin (8). Purple crystal powder, R_f 0.15 (eluent—tetrachloromethane–acetone, 5 : 1). IR spectrum (KBr), ν, cm^{-1}: 3502 (OH), 3318 (NH), 2870 (CH_3), 2955, 1597 (C=C), 1498, 1467, 1333, 1240, 1182, 1030, 966, 800, 733. ^1H NMR spectrum ($CDCl_3$), δ_H, ppm: –2.73 br.s (2H, NH), 4.10 s (6H, OCH_3), 5.96 s (1H, 5-ArOH), 7.33 s (2H, $ArH^{2'',6''}$), 7.81 br.s (9H, 10,15,20-$PhH^{3''',4''',5'''}$), 8.08 d (2H, 5-$ArH^{3',5'}$, J_{HH} = 8.2 Hz), 8.12 s (1H, NH), 8.25–8.29 m (8H, 5-$ArH^{2',6'}$,10,15,20-$PhH^{2''',6'''}$), 8.89 br.s (6H, $H^{2,8,12,13,17,18}$), 8.93 d (2H, $H^{3,7}$, J_{HH} = 4.6 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 56.74 (OCH_3), 104.54 ($ArC^{2'',6''}$), 118.41(5-$ArC^{3',5'}$), 120.20($C^{5,10,15,20}$), 126.70(10,15,20-$PhC^{3''',5'''}$),.74 (10,15,20-$PhC^{4'''}$), 130.51–131.93 ($C^{\alpha,\beta}$), 134.57, 135.23 (5-$ArC^{2',6'}$, 10,15,20-$PhC^{2''',6'''}$, 5-$ArC^{4'}$), 137.79 (5-$ArC^{1'}$), 138.38 и 138.55 ($ArC^{1''}$, $ArC^{4''}$), 142.19 (10,15,20-$PhC^{1'''}$), 147.18 ($ArC^{3'',5''}$), 165.80 (NHCOAr). EAS (CH_2Cl_2), λ_{max}, nm (*I*, %): 645.5(1), 591.0(1), 551.5(1), 516.0(3), 419.5(100). Mass spectrum (ESI), *m*/*z*: 810.5 $[M + H]^+$ (calculated for $C_{53}H_{40}N_5O_4$: 810.3).

5-[4'-(*N*,*N*-Dimethylformamidino)phenyl]-10,15,20-triphenylporphin (9). Purple crystal powder, R_f 0.25 (eluent—tetrachloromethane–acetone, 5 : 1). IR spectrum (KBr), ν, cm^{-1}: 3318 (N–H), 2924, 1595 (C=C), 1697, 1636 (C=N), 1074 (H_3C–N), 1518, 1469, 1350, 1180, 1026, 968, 800, 731. ^1H NMR spectrum ($CDCl_3$), δ_H, ppm: –2.71 br.s (2H, NH), 3.25 s [6H, $N(CH_3)_2$], 7.52 d (2H, 5-$ArH^{3',5'}$, J_{HH} = 8.2 Hz), 7.80 br.s (9H, 10,15,20-$PhH^{3'',4'',5''}$), 7.99 s (1H, N=CHN), 8.17 d (2H, 5-$ArH^{2',6'}$, J_{HH} = 8.2 Hz), 8.26 d (6H, 10,15,20-$PhH^{2'',6''}$, J_{HH} = 5.5 Hz), 8.88 br.s (6H, $H^{2,8,12,13,17,18}$), 8.93 d (2H, $H^{3,7}$, J_{HH} = 4.6 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 38.25 (CH_3), 119.48 (5-$ArC^{3',5'}$), 120.02 and 120.86 ($C^{5,10,15,20}$), 126.67 (10,15,20-$PhC^{3'',5''}$), 127.68 (10,15,20-$PhC^{4''}$), 130.47–131.83 ($C^{\alpha,\beta}$), 134.58 (10,15,20-$PhC^{2'',6''}$), 135.53 (5-$ArC^{2',6'}$, 5-$ArC^{4'}$), 138.65 (5-$ArC^{1'}$), 142.30 (10,15,20-$PhC^{1''}$), 151.52 (N=CH). EAS (CH_2Cl_2), λ_{max}, nm (*I*, %): 647.0(1), 590.0(1), 551.5(1), 515.5(4), 419.0(100). Mass spectrum (ESI), *m*/*z*: 685.8 $[M + H]^+$ (calculated for $C_{47}H_{37}N_6$: 685.3).

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CONFLICT OF INTERESTS

Autor declare no conflict of interest.

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