

Photosensitizers

Peripherally and Axially Carboxylic Acid Substituted Subphthalocyanines for Dye-Sensitized Solar Cells

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Abstract: A series of subphthalocyanines (SubPcs) bearing a carboxylic acid group either at the peripheral or axial position have been designed and synthesized to investigate the influence of the COOH group positions on the dye-sensitized solar cell (DSSC) performance. The DSSC devices based on

Introduction

Porphyrinoid dyes have a high molar extinction coefficient in the red/near-infrared region and therefore they have recently received much attention as the alternative to Ru-based dyes for their application in the field of dye-sensitized solar cells (DSSCs). Among them, a very high efficiency of up to 11% has been achieved by rational design of a push-pull porphyrin dye bearing an electron-donating diarylamino group at one meso position opposite to the binding 4-ethynylbenzoic acid moiety.^[1] A record power conversion efficiency in this family of porphyrin sensitizers has been recently reported by the same authors using a related porphyrin dye (YD2-o-C8) and an organic dye as co-sensitizer.^[2] These results demonstrate that a careful choice of the appropriate substituted porphyrinoids may yet offer a feasible alternative the most commonly used ruthenium dyes. Unfortunately, the photophysical stability of these porphyrin dyes is not very high, but these results are the most important proof of concept for future applications of porphyrinoids in DSSCs. On the other hand, phthalocyanines (Pc),

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SubPcs with axially substituted carboxylic acid groups showed low photovoltaic performance, whereas peripherally substituted one exhibited higher power conversion efficiency owing to improved injection from LUMO of SubPcs to the TiO_2 conduction band.

which are synthetic analogues of porphyrin, have been widely used as sensitizers because of their improved light-harvesting properties in the far red- and near-IR spectral regions and their extraordinary robustness.^[3] However, efficiency values of Pcbased DSSCs are in general below those made of their porphyrin relatives owing to a lack of absorption in the visible region. Nevertheless, the performance of Pc-based solar cells has been recently improved up to 5.9% by careful modifications of Pc structures.^[4]

The chemical flexibility of Pcs from the structural point of view allows the formal replacement of one or more isoindol units by other hetero- or carbocycles. This fact has been exploited in the preparation of novel Pc derivatives with different absorption properties to match the terrestrial solar emission spectrum. For instance, the formal removal of one isoindol unit from the Pc skeleton leads to the SubPc analogues. Subphthalocyanines (SubPcs)^[5] are Pc analogues comprising a 14- π electron nonplanar aromatic macrocycle consisting of three diiminoisoindole units N-fused around a central boron atom. In contrast with their related congeners, namely the planar Pcs, SubPcs possess a peculiar conical structure, which provides them with relatively high solubility and low tendency to aggregate. The important photophysical advantage of this class of compounds is based on their strong light absorption properties in the visible region (500-700 nm), which makes them an effective light harvesting material for artificial photosynthetic systems.^[6] Additionally, their electronically rich π -conjugated system and lower oxidation potential render them an excellent material for the production of solution-processed small-molecule OPVs.^[7] For instance, Verreet et al. have reported efficient organic photovoltaic cells with a power conversion efficiency of 4% by using a fluorinated fused subphthalocyanine dimer as a deep-red absorbing acceptor.^[8] In this regard, SubPcs have appeared as an alternative active-layer component in photovoltaic devices owing to the high open-circuit voltage (V_{oc}) values obtained by their introduction. Even though SubPcs

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have proven to be promising candidates as donor material for small-molecule organic solar cells, there has been no report on the immobilization of SubPcs on nanocrystalline TiO₂ to date. The characteristic features of SubPcs, therefore, encouraged us to investigate dye-sensitized solar cells using SubPcs as a light harvesting material.

In this context, the work presented herein is focused on the synthesis of new SubPc sensitizers (Figure 1) bearing a carbox-



Figure 1. Molecular structure of subphthalocyanines designed for DSSCs.

ylic acid group located either at the peripheral or axial positions. The photovoltaic performance of SubPcs in DSSCs was tested for the first time and the results provide a comparison of photovoltaic properties of SubPcs with carboxylic acid groups appended axially and peripherally.

Results and Discussion

Synthesis

Subphthalocyanines are formed by cyclotrimerization of phthalonitriles in the presence of boron reagents in a high-boilingpoint solvent, such as *p*-xylene.^[5] Among the different boron reagents, BCl₃ has been the more widely used. In general, the axial functionalization of SubPcs with nucleophiles such as phenol derivatives not only facilitates their purification by column chromatography separation, but also prevents hydrolysis during the chromatographic work up in silica gel, as is sometimes the case of bromo- or chloro-substituted SubPcs. On the other hand, functionalization of the peripheral benzene ring of the SubPc is somewhat difficult owing to its chemical instability. Indeed, the SubPc ring is frequently destroyed in the presence of a nucleophile at high temperatures or in basic media. Nevertheless, several metal-catalyzed reactions have been reported by our group on the coupling of peripherally iodine-substituted SubPcs with terminal alkynes.^[6b-d]

The synthesis of SubPcs 1 and 2, peripherally substituted with a terminal carboxylic acid group was, thus, carried out in two steps. First, di(*tert*-butyl)iodoSubPc 6 was synthesized and then the corresponding acid derivatives were obtained by means of a Sonogashira catalytic cross-coupling reaction with the appropriate alkyne, namely propargylic acid and 4-ethynyl-



benzoic acid. SubPc **6** was prepared by a statistical condensation reaction of 4-iodophthalonitrile^[9] and 4-*tert*-butylphthalo-

nitrile (1:2 molar ratio) in the presence of BCl₃, followed by substitution of the axial chlorine atom with 4-*tert*-butylphenol

in toluene. After purification by column chromatography, compound **6** was obtained in 12% yield, (Scheme 1). SubPcs **1** and

Scheme 1. Synthesis of subphthalocyanines (SubPcs) 6, 1, and 2.

2 were prepared by Sonagashira coupling reaction between iodoSubPc **6** and the corresponding carboxylic acid derivative. Both reactions were carried out in DMF in the presence of [PdCl₂(PPh₃)₂] as a catalyst, triethylamine as the base, and a catalytic amount of copper iodide. The purification of the crude material by column chromatography allowed the isolation of carboxySubPcs from the remaining iodoSubPc. SubPc **1** and **2** were obtained in 43% and 48% yields, respectively, based on the recovered SubPc **6**. SubPcs **1**, **2**, and **6** are each mixture of two constitutional isomers, which could not be separated by column chromatography.

Figure 2 displays the UV/Vis spectra of SubPc **1** and **2**, which are very similar, showing the Q band at 580 nm, together with a shoulder of vibronic origin.

The precursor **8** of the axially substituted SubPc **3** was prepared in an overall yield of 76% by a cyclotrimerization reaction of tetrafluorophthalonitrile in the presence of boron trichoride, followed by in situ substitution reaction of the chloro-SubPc intermediate with *m*-hydroxybenzaldehyde in toluene (Scheme 2). SubPc **8** was converted to SubPc **3** in 90% yield by oxidation with sodium chlorite in the presence of sulfamic acid as hypochlorite scavenger.

The synthesis of thioether-substituted SubPcs **4** and **5** was carried out as outlined in Scheme 3. Butyl and *tert*-butyl phenyl (alkyl and a bulky non-aggregating group, respectively) were chosen as radicals on the sulfur atoms. Dicyano compounds **9** and **10** were obtained in 72% and 80% yields, respectively, by nucleophilic aromatic substitution of 4,5-dichlor-ophthalonitrile^[10] with butanothiol and *tert*-butylthiophenol. Cylotrimerization of the corresponding phthalonitrile in presence of BCl₃, followed by in situ substitution of axial chlorine with 3-hydroybenzoic acid directly afforded SubPcs **4** and **5** in 42 and 27% yield, respectively.





Figure 2. UV/Vis spectra of SubPc 1 and 2 in $CHCI_3$ (ca. 1.10^{-5} m).



Scheme 2. Synthesis of SubPcs 8 and 3.



Scheme 3. Synthesis of SubPcs 4 and 5.

The UV/Vis absorption spectra for axially carboxySubPcs are shown in Figure 3. SubPcs 4 and 5 bearing electron-donating group revealed a strong bathochromic shift of their Q band (ca. 30 nm) with respect to acceptor SubPc 3.

All of the compounds were characterized by MALDI-TOF, ¹H NMR, UV/Vis, and IR spectroscopy. Unlike typical broadened peaks observed in the 1H NMR spectra of phthalocyanines that are due to the tendency of their π -system to form aggregates,







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Figure 3. UV/Vis spectra of SubPc 3, 4, and 5 in $CHCl_3$ (ca. 1.10^{-5} M).

SubPcs gave rise to well-resolved spectra in CDCl₃. All aromatic protons appear between 9.5-7.0 ppm, with the exception of the axial phenoxy ligand, the signals of which are shifted upfield, which is due to the strong ring current produced by the aromatic core.

Photovoltaic studies

Tables 1 and 2 summarize the I-V (short-circuit currents J_{scr} open-circuit voltages V_{oc}, fill factors FF, and conversion efficiencies η) of the peripherally and axially substituted carboxy-SubPcs in DSSCs, respectively. Owing to the cone-shaped geometry of SubPcs, which contrasts with the flat structure of Pcs, SubPcs have a remarkably lower aggregation tendency; therefore, the addition of coadsorbant does not influence the photovoltaic performance. All of the SubPcs dye solutions

Table 1. Photovoltaic performance of SubPc 1 and 2 in the presence of different electrolytes.									
Dye	Electrolyte	$J_{\rm sc}$ [mA/cm ²]	V _{oc} [mV]	FF	η [%]				
1	959	0.32	542	0.647	0.11				
	960	0.94	532	0.715	0.36				
	AY2	5.36	347	0.550	1.03				
	AY3	6.17	357	0.599	1.32				
2	959	0.19	547	0.639	0.07				
	960	0.55	519	0.727	0.21				
	AY2	5.5	343	0.585	1.12				
	AY3	4.9	347	0.622	1.08				

Table 2. Photovoltaic performance of SubPc 3, 4, and 5.									
Dye	Electrolyte	$J_{\rm sc}$ [mA/cm ²]	V _{oc} [mV]	FF	η [%]				
3	A6986	0.193	338	0.700	0.05				
	AY3	0.308	253	0.582	0.05				
4	A6986	0.536	372	0.718	0.14				
	AY3	2.243	275	0.611	0.38				
5	A6986	0.325	400	0.729	0.09				
	AY3	0.963	292	0.616	0.17				



were prepared in THF at a concentration of 0.1 mm. The film thickness of transparent TiO_2 and light-scattering layer were 7 μ m and 4 μ m, respectively. Table 1 shows the photovoltaic performance of dyes 1 and 2 in DSSC using different electrolytes (see the Supporting Information for the composition of the liquid electrolytes).

The devices using electrolyte 959 gave a $V_{\rm oc}$ of around 540 mV for both dyes. However, very low short-circuit photocurrent densities (J_{sc}) were obtained, and as a consequence resulted in lower power conversion efficiencies. Addition of 0.05 м Lil to the electrolyte 959 (coded as 960), the efficiencies obtained were three times higher than in the previous cells for both SubPcs owing to the increased J_{sc} . This can be attributed to the presence of Li⁺ in electrolyte 960, which caused a drop in the photovoltage as a result of the downward shift of the conduction band of the titania and hence an increase in the J_{sc} . As addition of Lil increased the J_{sc} value, an electrolyte employing 1 M Lil and 0.05 M I₂ (coded as AY2) was used, and this resulted in higher short-circuit photocurrent density of 5.3 and 5.5 mA/cm^2 for SubPc 1 and 2, respectively, which are more than 10 times higher than that obtained with 959 electrolyte, whereas the V_{oc} was lower for both dyes and this could be attributed to the downward shift of the conduction band of the titania owing to the lithium ions, as observed previously.^[11] Finally, by using AY3 electrolyte, which is a mixture of 0.5 M Lil and 0.5 M Nal, the power conversion efficiency of cells sensitized with SubPc 1 and 2 reached 1.32 and 1.08%, respectively. Figure 4 shows the I-V curves obtained with the electrolyte AY3.



Figure 4. I–V curves obtained with the Subpcs 1 (——) and 2 (----) with the electrolyte AY3 containing 0.5 m Lil, 0.5 m Nal, and 0.05 m I₂ in acetonitrile.

The power conversion efficiencies (η) of DSSCs based on SubPcs **3**, **4**,and **5** were found to be very low owing to mainly lower photocurrents (see Table 2). The use of AY3 electrolyte improved the J_{sc} , which are however still lower than those of SubPc **1** and **2**.

Conclusion

A series of new axially and peripherally carboxylic acid substituted SubPcs was prepared and incorporated into DSSC devices. Power conversion efficiencies were found to be very low with axially carboxySubPcs. The possible reason for low efficiency could be a mismatch between the TiO₂ conduction band and the LUMO of SubPc and the lack of electronic communication between the π -conjugated chromophore and the anchoring group owing to the presence of the boron atom. On the other hand, SubPc derivatives bearing carboxyl groups at peripheral positions 1 and 2 exhibited a power conversion efficiency of ca. 1.32% and 1.08%, respectively. These results are promising and instructive considering that it is the first report on SubPc-based DSSCs. Further modification of SubPcs by peripherally substituting them with other donor groups/ and peripherally anchoring groups patterns could be useful to improve these molecules as photosensitizers for DSSC applications. The research directed on these lines are undergoing in our group.

Experimental Section

4'-tert-Butylphenoxy[2(3),16(17)-di(tert-butyl)-9iodosubphthalocyaninato]boron(III) (mixture of regioisomers; 6)

BCl₃ (7.5 mL, 1 M solution in p-xylene) was added to a mixture of 4tert-butylphthalonitrile (578 mg, 3.14 mmol) and 4-iodophthalonitrile (400 mg, 1.57 mmol) under an argon atmosphere. The reaction mixture was refluxed at 150°C for 2 h. After cooling down to room temperature, the unreacted BCl₃ and solvent were quickly removed in vacuo. 4-tert-butylphenol (943 mg, 6.28 mmol), dry toluene (4 mL), and then TEA (0.2 mL, 1.6 mmol) were added to the crude mixture and stirring was continued at 110°C for 3 h. The solvent was removed by vacuum distillation and the solid was washed with a mixture of methanol/water (4:1). The compound was purified by column chromatography on silica gel (hexane/dioxane 8:1) as eluent to yield 6 (186 mg, 0.18 mmol) as a reddish solid. Yield: 12%. ¹H NMR (CDCl₃, 300 MHz): $\delta = 9.2$ (d, J = 6 Hz, 1H), 8.87 (d, J =9 Hz, 2 H), 8.78–8.72 (m, 2 H), 8.6–8.4 (m, 1 H), 8.1 (d, J=9 Hz, 1 H), 7.9 (d, J=9, 2H) 6.7 (d, J=9 Hz, 2H), 5.2 (d, J=9 Hz, 2H), 1.5 (s, 18H), 1.07 ppm (s, 9H); FTIR (film): $\tilde{\nu} = 2961$, 2866, 1618, 1605, 1510, 1456, 1177, 1068, 885, 762 cm⁻¹; UV/Vis (CHCl₃): λ_{max} (log ε) = 571 (4.64), 513 (4.08), 315 (4.34), 268 nm (4.46); HRMS (MALDI-TOF, DCTB): *m/z*: calcd for C₄₂H₄₀BIN₆O [*M*⁺]: 781.2432; found: 781.2472.

4'-tert-Butylphenoxy [2(3),16(17)-di(tert-butyl)-9-carboxyethynyl subphthalocyaninato)]boron(III) (1) and 4'-tert-butylphenoxy [2(3),16(17)-di(tert-butyl)-9-(4''-ethynylbenzoic acid) subphthalocyaninato]boron(III) (2)

General procedure: A mixture of SubPc **6** (50 mg, 0.064 mmol), $[PdCl_2(PPh_3)_2]$ (4.5 mg, 0.006 mmol) and CuI (0.6 mg, 0.003 mmol) was stirred in the mixture of DMF/TEA (6:1) (3.5 mL) under argon. The corresponding alkynyl carboxylic acid derivative (0.2 mmol) was added while the temperature was kept at 0 °C. The reaction was then stirred at room temperature for 2 h. Water was then added and the mixture was extracted with EtOAc. The combined organic layers were dried over MgSO₄ and evaporated in vacuo.

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The solid residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH 10:1).

SubPc **1** (12 mg, 0.016 mmol) was obtained as a reddish solid. Yield: 43% (based on the recovered starting iodoSubPc). ¹H NMR (300 MHz, CDCl₃): δ =9.3 (s, 1 H), 9.2 (s, 2 H), 9.1–8.9 (m, 3 H), 8.4–8.2 (m, 3 H), 6.9 (d, *J*=9 Hz, 2 H), 5.6 (d, *J*=9 Hz, 2 H), 1.7 (s, 18 H), 1.3 ppm (s, 9 H); FTIR (film): $\tilde{\nu}$ =3298, 2961, 2921, 2853, 2218, 1730, 1609, 1474, 1366, 1258, 1177, 1055, 812, 798, 758cm⁻¹; UV/Vis (CHCl₃): λ_{max} (log ε) = 580 (4.57), 570 (4.49), 542 (4.26), 515 (4.11), 316 (4.40), 268 nm (4.58); HRMS (MALDI-TOF, DCTB): *m/z*: calcd for C₄₅H₄₁BN₆O₃ [*M*⁺]: 723.3364; found: 723.3401.

SubPc **2** (17 mg, 0.021 mmol) was obtained as a reddish solid. Yield: 48% (based on the recovered starting iodoSubPc). ¹H NMR (300 MHz, CDCl₃): δ =9.4 (s, 1H), 9.2–9.0 (m, 5H), 8.4 (d, J=9 Hz, 2H), 8.3–8.2 (m, 3H), 7.9 (d, J=9 Hz, 2H), 6.9 (d, J=9 Hz, 2H), 5.5 (d, J=9 Hz, 2H), 1.4 (s, 18H), 1.08 ppm (s, 9H); FTIR (film) $\tilde{\nu}$ =3379, 2961, 2934, 2893, 1726, 1699, 1618, 1510, 1470, 1267, 1254, 1124, 1097, 806, 760 cm⁻¹; UV/Vis (CHCl₃): λ_{max} (log ε) = 583 (4.68), 568 (4.61), 543 (4.35), 523 (4.22), 310 (4,57), 271 nm (4.58); HRMS (MALDI-TOF, DCTB): *m/z*: calcd for C₅₁H₄₅BN₆O₃ [*M*⁺]: 799.3677; found: 799.3744.

3'-Formylphenoxy-[1,2,3,4,8,9,10,11,15,16,17,18-dodeca-fluoro subphthalocyaninato]boron(III) (8)

BCl₃ (5 mL, 1 M solution in *p*-xylene) was added to tetrafluorophthalonitrile (5 mmol) under argon atmosphere. The reaction mixture was refluxed for 30 min. After cooling down to room temperature, the unreacted BCl₃ and solvent were quickly removed in vacuo. 3-Hydroxybenzaldehyde (2.5 mmol) and dry toluene (2 mL) were added to crude mixture and stirring was continued at 110 °C for 2 h. The reaction mixture was cooled down to room temperature, the solvent was evaporated and the solid residue was washed with a mixture of methanol/water (4:1). The compound was then purified by column chromatography on silica gel using a 20:1 mixture of toluene/THF as eluent. Compound 8 was further purified by washing with hexane, giving a dark magenta solid. Yield: 76%. ¹H NMR (300 MHz, CDCl₃): $\delta = 9.63$ (s, 1 H), 7.2 (dd, $J_0 = 7.6$ Hz, $J_m =$ 1.6 Hz, 1 H), 7.0 (dd, $J_0 = 7.6$ Hz, $J_{0'} = 8.2$ Hz, 1 H), 5.9 (br s, 1 H), 5.57 ppm (dd, $J_{o'} = 8.2$ Hz, $J_m = 1.6$ Hz, 1 H). FTIR (KBr): $\tilde{\nu} = 1682$, 1533, 1483, 1266, 1112, 1091, 1054 cm⁻¹; UV/Vis (CHCl₃): λ_{max} (log ε) = 571 (4.6), 554 (sh), 527 (sh), 307 (4.0), 269 nm (4.1); MS (LSI-MS, *m*-NBA): *m*/*z*: 748 [*M*]⁺. HRLSI-MS (C₃₁H₅N₆O₃F₁₂B): *m*/*z*: calcd for [*M*⁺]: 748.0012; found: 748.0006.

3'-Carboxyphenoxy-[1,2,3,4,8,9,10,11,15,16,17,18-dodecafluorosubphthalocyaninato]boron(III) (3)

NaClO₂ (26 mg, 0.25 mmol) was added slowly to a solution of aldehyde **8** (520 mg, 0.71 mmol) in acetone (400 mL). A sulfamic acid solution (22 mg, 0.25 mmol) in deionized water (50 mL) was then added in one portion. The reaction mixture was stirred at 0 °C for 30 min. Once the oxidation was completed (checked by TLC), the solution was poured into cold water (400 mL). The precipitate was centrifuged and washed with water/methanol (2:1). Compound **3** was obtained as a dark magenta solid. Yield: 90%. ¹H NMR (400 MHz, CDCl₃): δ = 7.5–7.4 (m, 1H), 6.9–6.8 (m, 1H), 6.1 (brs, 1H), 5.6–5.4 ppm (m, 1H). FTIR (KBr): $\tilde{\nu}$ = 1682, 1533, 1483, 1266, 1112, 1091, 1054 cm⁻¹; UV/Vis (CHCl₃): λ_{max} (log ε) = 571 (4.9), 554 (4.6), 527 (4.3), 307 (4.5), 269 nm (4.4); HRMS (MALDI-TOF): *m/z*: calcd for C₃₁H₅N₆O₃F₁₂B [*M*⁺]: 747.0354; found: 746.8889.

3'-Carboxyphenoxy-[2,3,9,10,16,17-

thiobutylsubphthalocyaninato]boron(III) (4) and 3'-carboxy-phenoxy-[2,3,9,10,16,17-tert-

butylthiophenylsubphthalocyaninato]boron(III) (5)

General procedure: A solution of corresponding phthalonitrile (5 mmol) in the presence of BCl₃ (5 mL, 1 \bowtie solution in *p*-xylene) was heated under reflux for 30 min. After cooling down to room temperature, the unreacted BCl₃ and solvent were quickly removed in vacuo. 3-hydroybenzoic acid (2.5 mmol) and dry toluene (2 mL) were added to crude mixture and stirring was continued at 110 °C for 12 h. The reaction mixture was cooled down to room temperature, the solvent was removed under vacuum. The solid residue was directly subjected to column chromatography on silica gel using a 3:1 mixture of hexane/EtOAc as eluent.

SubPc **4** was obtained as a deep blue solid. Yield: 42%. ¹H NMR (400 MHz, CDCl₃): δ = 8.6 (s, 6 H), 7.4 (d, J = 8, 1 H), 6.9 (t, J = 8, 1 H), 6.2 (s, 1 H), 5.7 (d, J = 8, 1 H), 3.2–3.3 (m, 12 H), 1.8–1.7 (m, 12 H), 1.6–1.4 (m, 12 H), 1.0–0.8 ppm (m, 18 H); FTIR (KBr): $\tilde{\nu}$ = 2934, 2760, 1481, 1221, 1097, 1056, 904 cm⁻¹; UV/Vis (CHCl₃): λ_{max} (log ϵ) = 600 (4.9), 582 (4.7), 414 (4.4), 388 (4.5), 295 nm (4.8); HRMS (MALDI-TOF): m/z: calcd for C₅₅H₆₅N₆S₆O₃B [M^+]:1059.3565; found: 1059.3783.

SubPc **5** was obtained as a deep blue solid. Yield: 27%. ¹H NMR (400 MHz, CDCl₃): δ = 8.4 (s, 6H), 7.4 (brs, 24H), 7.3 (m, 1H), 6.8 (t, *J* = 8, 1H), 6.1 (s, 1H), 5.3 (d, *J* = 8, 1H), 1.3 ppm (m, 54H). FTIR (KBr); $\tilde{\nu}$ = 3437, 2912, 1702, 1625, 1497, 1376, 1098, 877 cm⁻¹; UV/ Vis (CHCl₃): λ_{max} (log ε) = 607 (5.0), 554 (4.5), 423 (4.4), 387 (4.5), 290 nm (4.9); HRMS (MALDI-TOF): *m/z*: calcd for C₉₁H₈₉N₆S₆O₃B [*M*⁺]: 1515.5441; found: 1515.5560.

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