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Synthesis and photochemical characteristics of novel tribenzoporphyrazines possessing peripherally annulated tetrahydrodiazepine and diazepine rings

Tomasz Goslinski [a,*], Jaroslaw Piskorz [b], Dawid Brudnicki [a], Andrew J.P. White [c], Maria Gdaniec [d], Wojciech Szczolko [a], Ewa Tykarska [a]

[a] Department of Chemical Technology of Drugs, Poznan University of Medical Sciences, Grunwaldzka 6, 60-780 Poznan, Poland
[b] Department of Inorganic and Analytical Chemistry, Poznan University of Medical Sciences, Grunwaldzka 6, 60-780 Poznan, Poland
[c] Department of Chemistry, Imperial College, London SW7 2AZ, United Kingdom
[d] Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland

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ABSTRACT

Novel tribenzoporphyrazines possessing peripherally annulated tetrahydrodiazepine and diazepine rings were synthesized and characterized, and the substituent effects on their absorption spectra in various solvents and on singlet oxygen generation were studied. Solvatochromic effects of tribenzoporphyrazines dissolved in a range of protic and aprotic solvents were evaluated by monitoring the changes in the UV–Vis spectra. The correlation between the Q-band shift towards longer wavelengths and the refractive index of the solvent indicated that the solvatochromic effects are mainly a result of solvation rather than coordination processes. The potential photosensitizing activity of novel tribenzoporphyrazines was evaluated by measuring the ability of singlet oxygen production, which is the result of the interaction between an activated photosensitizer and oxygen. This experiment proves promising photosensitizing activity of novel styryldiazepinotribenzoporphyrazine, which is an efficient singlet oxygen generator with a Φ_Δ value of 0.44, although this value is a little lower than that of zinc phthalocyanine.

1. Introduction

Porphyrazines (pzs), including tribenzoporphyrazines, are synthetic analogs of porphyrins, which are present in nature. Their structural modifications embrace metal inclusion to the macrocycle core and peripheral substitution, which results in a significant modulation of their electrochemical and optical properties. Peripherally modified pzs can be substituted in the β positions with sulfur, oxygen and nitrogen residues or have five-, six- and seven-membered rings bound to both β,β positions [1,2]. Porphyrazines have been investigated as sensitizers for photodynamic therapy [3], metal ion and gas sensors [4], precursors for optical data recording systems, electrochromic displays, magnetic, electronic and conductive materials for nanotechnology [5–9].

For more than 10 years Ercolani and Stuzhin [1,10,11] have reported the synthesis, characterization and applications of a new class of porphyrazines carrying peripherally annulated diazepine rings. The 1,4-diazepine ring, that contains six π-electrons annulated to the free-base porphyrazine and its numerous metal complexes, exists in the stable 6*H*-tautomeric form and has been considered as *quasi*-aromatic. Complexes of Mn(II) and Li(I) exist in the 1*H*-form, even after acidic solvation in CF_3COOH. These macrocycles are far from being entirely planar, and the mutual structural and electronic interaction between planar porphyrazine and non-planar diazepine rings is of great interest. Following Donzello et al. [12], the UV–Vis spectra of these macrocycles in basic, acidic and neutral media confirmed the multifaceted participation of the external diazepine rings through tautomeric and protonated forms to electron sharing within the entire metal-macrocycle framework. Non-linear optical investigations have shown that diazepinoporphyrazine complexes behave in solution like reverse-saturable absorbers (RSA), which show reduced transmittance with increased irradiation. Lately low-symmetry tribenzoporphyrazines with annulated 6*H*-1,4-diazepine rings have been synthesized and subjected to spectroscopic studies [13,14]. In addition to the studies embracing the diazepinoporphyrazines, Barrett and Hoffman [15] have published the synthesis, characterization and photochemistry of novel tetrahydrodiazepinoporphyrazine and its *seco*-derivative.

Donzello et al. [10] suggested that the physical properties of this new class of complexes can be modulated by operating appropriate substitutions in the 5, 6 and 7 positions of the external diazepine rings. This study aims to present a strategy leading to further functionalised diazepino- and tetrahydrodiazepinoporphyrazines. The newly synthesized tribenzoporphyrazines

* Corresponding author. Tel.: +48 61 854 66 33; fax: +48 61 854 66 39.
E-mail address: tomasz.goslinski@ump.edu.pl (T. Goslinski).

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were studied for the substituent effects on their absorption spectra in different solvents and on singlet oxygen generation.

2. Experimental

2.1. Synthesis

The known compounds ethyl 3-acetyl-4-oxopentanoate (**2a**) [16–18], ethyl 4-oxo-4-phenyl-3-(phenylcarbonyl)butanoate (**2b**) [19], 5-methyl-7-phenyl-6*H*-1,4-diazepine-2,3-dicarbonitrile (**9**) [20] and 5-[(*E*)-2-(4-methoxyphenyl)ethenyl]-7-phenyl-6*H*-1,4-diazepine-2,3-dicarbonitrile (**11a**) [21] were synthesized according to the literature procedures and their modifications.

2.1.1. 5,7-Dimethyl-6-ethoxycarbonylmethyl-6H-1,4-diazepine-2,3-dicarbonitrile (*4*)

Diketone **2a** (5.880 g, 31.60 mmol), diaminomaleonitrile **3** (3.420 g, 31.60 mmol) and oxalic acid dihydrate (0.200 g, 1.59 mmol) in benzene (63 mL) were refluxed under a Dean–Stark receiver for 41 h. The solvent was then evaporated and the residual solid was chromatographed (*n*-hexane–ethyl acetate, 7:3 to 7:4). Crystallization from *n*-hexane–ethyl acetate gave yellowish crystals of **4** (1.000 g, 12%): Mp 147–149 °C, R_f 0.42 (*n*-hexane–ethyl acetate, 1:1). IR (neat) cm^{-1}: 2987, 2927, 2223, 1731, 1446, 1173, 1022, 948, 878. ^1H NMR (400 MHz; $CDCl_3$) δ_H, ppm: 4.26 (q, 2H, ^3J = 7 Hz, CH_2CH_3), 3.27 (d, 2H, ^3J = 8 Hz, CH_2CO), 2.15 (s, 6H, 2 × CH_3), 1.90 (t, 1H, ^3J = 8 Hz, CH), 1.32 (t, 3H, ^3J = 7 Hz, CH_2CH_3). ^{13}C NMR (100 MHz; $CDCl_3$) δ_C, ppm: 169.6 (CO), 152.6, 122.0, 114.2, 61.9 (OCH_2), 53.8, 32.0, 22.2, 14.1 (CH_2CH_3). MS (EI) *m/z*: 258 $[M]^{+\cdot}$, 229 $[M-CH_3CH_2]^+$, 213 $[M-CH_3CH_2O]^+$, 185 $[M-CH_3CH_2OCO]^+$, 171 $[M-CH_3CH_2OCOCH_2]^+$. MS (ES) *m/z*: 259 $[M+H]^+$. HRMS (EI) *m/z*: 258.1116 (calc. for $[M]^{+\cdot}$ 258.1117). *Anal.* Calc. for $C_{13}H_{14}N_4O_2$: C, 60.45; H, 5.46; N, 21.69. Found: C, 60.53; H, 5.35; N, 21.55%.

Crystal data for **4**: $C_{13}H_{14}N_4O_2$, *M* = 258.28, monoclinic, $P2_1/c$, *a* = 9.0074(2), *b* = 13.4610(3), *c* = 11.5446(3) Å, β = 108.826(3)°, *V* = 1324.88(6) $Å^3$, *Z* = 4, D_c = 1.295 g cm^{-3}, μ(Mo Kα) = 0.09 mm^{-1}, colorless blocks, *T* = 173 K, OD Xcalibur 3 diffractometer, 4423 independent reflections, 3398 reflections with $I > 2\sigma(I)$, R_{int} = 0.022, θ_{max} = 32.3°, R_1(obs) = 0.039, wR_2(all) = 0.121, 174 parameters.

2.1.2. 5,7-Dimethyl-6-ethoxycarbonylmethyl-4,5,6,7-tetrahydro-1H-1,4-diazepine-2,3-dicarbonitrile (*5*)

$NaBH_4$ (0.204 g, 5.40 mmol) was added in three portions to a suspension of diazepine **4** (0.664 g, 2.57 mmol) in methanol (20 mL) at −5 °C over 45 min. The mixture was then stirred for another 1.5 h at room temperature. The solvent was evaporated and the residual solid was diluted with water (20 mL) and extracted with ethyl acetate (total amount 250 mL). Chromatography (*n*-hexane–ethyl acetate, 7:1 to 1:1) gave diazepine **5** (0.607 g, 90%): Mp 149–150 °C, R_f 0.82 (*n*-hexane–ethyl acetate, 2:3). IR (neat) cm^{-1}: 3342, 2984, 2209, 1730, 1536, 1460, 1277, 1175. ^1H NMR (300 MHz; $CDCl_3$) δ_H, ppm: 4.13 (q, 2H, ^3J = 7 Hz, CH_2CH_3), 3.48 (bs, 2H, 2 × NH), 2.99 (q, 2H, ^3J = 6 Hz, 2 × NHC*H*), 2.22 (s, 3H, $CHCH_2CO$), 1.26 (t, 3H, ^3J = 7 Hz, CH_2CH_3), 1.22 (d, 6H, ^3J = 7 Hz, 2 × $CHCH_3$). ^1H NMR (400 MHz; DMSO-d_6) δ_H, ppm: 5.95 (s, 2H, 2 × NH), 4.04 (q, 2H, ^3J = 7 Hz, CH_2CH_3), 2.88 (q, 2H, ^3J = 6 Hz, 2 × NHC*H*), 2.03 (overlapped, 2H, CH_2CO), 2.01 (overlapped, 1H, $CHCH_2$), 1.17 (t, 3H, ^3J = 7 Hz, CH_2CH_3), 1.08 (d, 6H, ^3J = 6 Hz, 2 × $CHCH_3$). ^{13}C NMR (75 MHz; $CDCl_3$) δ_C, ppm: 173.6 (CO), 116.4, 109.4, 60.8, 58.3, 47.1, 26.0, 20.7, 14.1 (CH_2CH_3). ^{13}C NMR (100 MHz; DMSO-d_6) δ_C, ppm: 173.3 (CO), 117.2, 107.9, 60.0, 57.3, 48.0, 25.8, 19.9, 14.0 (CH_2CH_3). MS (ES) *m/z*: 261 $[M-H]^-$, 285 $[M+Na]^+$. *Anal.* Calc. for $C_{13}H_{18}N_4O_2$: C, 59.53; H, 6.92; N, 21.36. Found: C, 59.32; H, 6.56; N, 21.17%.

2.1.3. 6-Ethoxycarbonylmethyl-4,5,6,7-tetrahydro-1,4,5,7-tetramethyl-1H-1,4-diazepine-2,3-dicarbonitrile (*6*)

NaH (60% in mineral oil, 0.068 g, 1.7 mmol) was suspended in DMF (15 mL) and stirred for 30 min at −15 °C. Next, **5** (0.200 g, 0.763 mmol) in DMF (5 mL) was added over 30 min, and then the mixture was stirred for another 30 min. $(CH_3)_2SO_4$ (0.170 mL, 1.80 mmol) in DMF (2 mL) was added dropwise over 15 min at −15 °C. The mixture was stirred for 2 h, poured into ice water (50 mL) and then extracted with dichloromethane (3 × 50 mL). The solvent was evaporated and the residual solid was chromatographed (*n*-hexane–ethyl acetate 7:1 to 7:3) to give yellowish crystals of *meso* compound **6** (0.180 g, 81%): Mp 69–70 °C, R_f 0.32 (*n*-hexane–ethyl acetate, 7:5). IR (neat) cm^{-1}: 2976, 2936, 2203, 1729, 1562, 1174, 1030. ^1H NMR (400 MHz; $CDCl_3$) δ_H, ppm: 4.18 (q, 2H, ^3J = 7 Hz, CH_2CH_3), 3.50 (dq, 2H, ^3J = 6 Hz, 2 × $CHCH_3$), 2.93 (s, 6H, 2 × NCH_3), 2.45 (m, 1H, $CHCH_2$), 2.36 (d, 2H, ^3J = 8 Hz, CH_2CO), 1.29 (t, 3H, ^3J = 7 Hz, CH_2CH_3), 1.19 (d, 6H, ^3J = 7 Hz, 2 × $CHCH_3$); ^{13}C NMR (100 MHz; $CDCl_3$) δ_C, ppm: 172.0 (CO), 115.1, 114.9, 61.0, 58.7, 39.4, 35.6, 32.7, 14.5, 14.2 (CH_2CH_3). MS (EI) *m/z*: 290 $[M]^{+\cdot}$. MS (ES): 313 $[M+Na]^+$, 329 $[M+K]^+$, 275 $[M-CH_3]^-$. HRMS (EI) *m/z*: 290.1737 (calc. for $[M]^{+\cdot}$ 290.1743). *Anal.* Calc. for $C_{15}H_{22}N_4O_2$: C, 62.05; H, 7.64; N, 19.30. Found: C, 62.11; H, 7.67; N, 19.21%.

Crystal data for **6**: $C_{15}H_{22}N_4O_2$, *M* = 290.37, orthorhombic, $Pca2_1$, *a* = 18.9315(7), *b* = 9.2846(3), *c* = 8.8695(3) Å, *V* = 1559.00(9) $Å^3$, *Z* = 4, D_c = 1.237 g cm^{-3}, μ(Mo Kα) = 0.09 mm^{-1}, colorless prism, *T* = 130 K, Xcalibur, Eos diffractometer, 2180 independent reflections, 1779 reflections with $I > 2\sigma(I)$, R_{int} = 0.025, θ_{max} = 25.3°, R_1(obs) = 0.033, wR_2(all) = 0.068, 195 parameters, 1 restraint.

2.1.4. Tetrakis(6-pentoxycarbonylmethyl-4,5,6,7-tetrahydro-1,4,5,7-tetramethyl-1H-1,4-diazepino)[2,3-b;2′,3′-g;2″,3″-l;2‴,3‴-q]porphyrazinatozinc(II) (*7*)

Diazepine **6** (0.196 g, 0.676 mmol), zinc acetate (0.062 g, 0.34 mmol), pentanol (2 mL) and DBU (0.100 mL, 0.676 mmol) were added together and stirred for 16 h at 130 °C. The solvent was then evaporated with toluene and the residual oil was chromatographed three times (*n*-hexane–ethyl acetate 7:3 to 1:1) to give a blue unseparable mixture of the diastereoisomeric porphyrazines **7** (0.017 g, 7%): R_f 0.21 (*n*-hexane–ethyl acetate 7:3). UV–Vis (dichloromethane) λ_{max}, nm (log ε): 348 (4.47), 560 (4.33). IR (neat) cm^{-1}: 2928, 1733, 1578, 1465, 1377, 1275, 1167. ^1H NMR (500 MHz; d_5-pyridine) δ_H, ppm: 4.26 (overlapped, 8H, 8 × $CHCH_3$), 4.24 (s, 24H, 8 × NCH_3), 4.17 (t, ^3J = 7 Hz, 8H, 4 × OCH_2), 3.16 (m, 4H, 4 × $CHCH_2$), 2.81 (m, 8H, 4 × CH_2CO), 1.56 (m, 8H, 4 × OCH_2CH_2), 1.52 (m, 24H, 8 × $CHCH_3$), 1.22 (m, 16H, 4 × $CH_2CH_2CH_3$), 0.79 (t, ^3J = 6 Hz, 12H, 4 × CH_2CH_3). ^{13}C NMR (126 MHz; d_5-pyridine) δ_C, ppm: 173.6 (CO), 152.1, 152.0, 136.7, 136.3, 64.5, 60.5, 41.9, 38.5, 32.3, 28.4, 28.0, 22.2, 16.7, 13.8 (CH_2CH_3). MS (MALDI TOF) *m/z* 1394 $[M + H]^+$.

2.1.5. (6-Pentoxycarbonylmethyl-4,5,6,7-tetrahydro-1,4,5,7-tetramethyl-1H-1,4-diazepino)[2,3-q]tribenzo[b,g,l]porphyrazinatozinc(II) (*8*)

Diazepine **6** (0.102 g, 0.350 mmol), phthalonitrile (0.448 g, 3.50 mmol), zinc acetate (0.353 g, 1.92 mmol) and DBU (0.575 mL, 3.85 mmol) were added to pentanol (3 mL) and refluxed for 24 h. The reaction mixture was cooled to room temperature and the solvent was evaporated with toluene (2 × 50 mL). The residual oil was chromatographed twice (*n*-hexane–ethyl acetate 7:5 and *n*-hexane–ethyl acetate 7:1 to 7:1.5) to give the light blue porphyrazine **8** (0.036 g, 13%): R_f 0.70 (*n*-hexane–ethyl acetate, 7:5). UV–Vis (DMSO): λ_{max}, nm (log ε): 349 (4.21), 667 (4.31). ^1H NMR (400 MHz; d_5-pyridine) δ_H, ppm: 9.75 (m, 4H, ArH), 9.54 (d, 2H, ^3J = 6 Hz, ArH), 8.18 (m, 6H, ArH), 4.51 (s, 6H, 2 × NCH_3), 4.38 (dq, 2H, ^3J = 7 Hz, 2 × $CHCH_3$), 4.18 (t, 2H, ^3J = 7 Hz, OCH_2), 3.26

(m, 1H, $CHCH_2$), 2.92 (d, 2H, ^3J = 7 Hz, CH_2CO), 1.68 (d, 6H, ^3J = 7 Hz, 2 × $CHCH_3$), 1.55 (p, 2H, ^3J = 7 Hz, OCH_2CH_2), 1.18 (m, 4H, $CH_2CH_2CH_3$), 0.74 (t, 3H, ^3J = 7 Hz, CH_2CH_3). ^{13}C NMR (100 MHz; d_5-pyridine) δ_C, ppm: 173.8 (CO), 154.6, 154.1, 153.9, 153.0, 139.4, 139.2, 139.0, 136.8, 129.6, 129.5, 64.8, 61.5, 42.7, 39.5, 32.4, 28.6, 28.2, 22.4, 17.2, 14.0 (CH_2CH_3). MS (MALDI TOF) *m/z* 781 $[M+H]^+$.

2.1.6. 5-[(E)-2-(2,4-Dimethoxyphenyl)ethenyl]-7-phenyl-6H-1,4-diazepine-2,3-dicarbonitrile (**11b**)

Dinitrile **9** (0.200 g, 0.848 mmol), 2,4-dimethoxybenzaldehyde (0.141 g, 0.848 mmol), piperidine (4 drops) and benzene (8.5 mL) were refluxed for 16 h. The color of the reaction mixture changed from yellow to red-brown. After the solvent had been evaporated, the dry residue was chromatographed in dichloromethane and crystallized from dichloromethane–*n*-hexane to give a bright red precipitate (yellowish-orange after being dissolved in dichloromethane) of **11b** (0.135 g, 41%): Mp 233–235 °C dec, R_f 0.31 (*n*-hexane–ethyl acetate, 7:5), 0.20 (dichloromethane). UV–Vis (dichloromethane) λ_{max}, nm (log ε): 252 (4.35), 311 (4.33), 427 (4.36). ^{1}H NMR (400 MHz; DMSO-d_6) δ_H, ppm: 8.18 (d, 2H, ^3J = 7 Hz, ArH); 7.92 (d, 1H, ^3J = 16 Hz, =CH), 7.61 (t, 2H, ^3J = 8 Hz, ArH), 7.54 (t, 2H, ^3J = 8 Hz, ArH), 6.97 (d, 1H, ^3J = 16 Hz, =CH), 6.59 (s, 1H, ArH), 6.57 (d, 1H, ArH), 5.74 (bs, 1H, N=C–CH^{eq}), 3.88 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 2.17 (bs, 1H, N=C–CH^{ax}). ^{13}C NMR (100 MHz; DMSO-d_6) δ_C, ppm: 163.5, 160.0, 151.9, 151.1, 140.6, 133.0, 132.9, 130.8, 130.5, 129.0, 123.6, 122.0, 121.8, 116.2, 116.0, 115.9, 106.6, 98.3, 55.8, 55.6, 39.5^h. MS (ES) *m/z*: 381 $[M-H]^-$, 383 $[M+H]^+$, 405 $[M+Na]^+$. *Anal.* Calc. for: $C_{23}H_{18}N_4O_2 \times 0.25H_2O$: C, 71.40; H, 4.82; N, 14.48. Found: C, 71.38; H, 4.59; N, 14.47%.

2.1.7. 5-Phenyl-7-[(E)-2-(3,4,5-trimethoxyphenyl)ethenyl]-6H-1,4-diazepine-2,3-dicarbonitrile (**11c**)

Dinitrile **9** (0.208 g, 0.882 mmol), 3,4,5-trimethoxybenzaldehyde (0.173 g, 0.882 mmol), piperidine (5 drops) and benzene (20 mL) were refluxed for 24 h. The color of the reaction mixture changed from yellow to red-brown. After the solvent had been evaporated, the dry residue was chromatographed using dichloromethane–methanol 10:1 and *n*-hexane–ethyl acetate 2:3. Next the solid residue was crystallized from *n*-hexane–ethyl acetate to give a bright red precipitate (yellowish-orange after being dissolved in dichloromethane) of **11c** (0.233 g, 64%): Mp 190 °C dec, R_f 0.82 (dichloromethane–methanol, 10:1), 0.47 (*n*-hexane–ethyl acetate, 2:3). UV–Vis (dichloromethane) λ_{max}, nm (log ε): 255 (4.29), 323 (4.28), 409 (4.34). ^{1}H NMR (400 MHz; DMSO-d_6) δ_H, ppm: 8.22 (d, 2H, ^3J = 7 Hz, ArH), 7.91 (d, 1H, ^3J = 16 Hz, =CH), 7.60 (m, 1H, ArH), 7.54 (t, 2H, ^3J = 7 Hz, ArH), 7.10 (d, 1H, ^3J = 16 Hz, =CH), 7.03 (s, 2H, ArH), 5.75 (s, 1H, N=C–CH^{eq}), 3.81 (s, 6H, 2 × OCH_3), 3.68 (s, 3H, OCH_3), 2.21 (s, 1H, N=C–CH^{ax}). ^{13}C NMR (100 MHz; DMSO-d_6) δ_C, ppm: 153.1, 151.3, 150.7, 145.5, 140.1, 133.2, 132.8, 130.5, 130.1, 129.0, 123.8, 123.4, 122.4, 116.0, 115.8, 106.1, 60.1, 56.0, 39.5^h. MS (ES) *m/z*: 413 $[M+H]^+$, 435 $[M+Na]^+$. *Anal.* Calc. for: $C_{24}H_{20}N_4O_3$: C, 69.89; H, 4.89; N, 13.58. Found: C, 69.65; H, 5.13; N, 13.30%.

2.1.8. {5-Phenyl-7-[(2E)-(3,4,5-trimethoxyphenyl)ethenyl]-6H-1,4-diazepino}[2,3-q]tribenzo[b,g,l]porphyrazinatomagnesium(II) (**12**)

Magnesium (0.063 g, 2.6 mmol), butanol (40 mL) and a catalytic amount of iodine were refluxed for 24 h. Then diazepine **11c** (0.100 g, 0.243 mmol) and phthalonitrile (0.307 g, 2.40 mmol) were added and the reaction mixture was refluxed for 21 h. After Celite filtration, butanol was evaporated off with toluene. The solid residue was chromatographed (dichloromethane–methanol 35:1 to 10:1). Subsequent chromatography using a reversed phase column (methanol–tetrahydrofuran 10:1) gave **12** (0.028 g, 14%). R_f 0.38 (dichloromethane–methanol, 20:1), R_f (reversed phase) 0.30 (methanol–tetrahydrofurane, 10:1). UV–Vis (DMSO) λ_{max}, nm (log ε): 358 (4.55), 658 (4.52), 692 (4.55). ^{1}H NMR (400 MHz; d_5-pyridine) δ_H, ppm: 9.72 (s, 6H, ArH), 8.95 (d, 2H, ^3J = 7 Hz, ArH), 8.26 (d^h, 1H, =CH), 8.21 (m, 2H, ArH), 8.16 (m, 2H, ArH), 8.10 (m, 2H, ArH), 7.89 (d, 1H, ^3J = 16 Hz, =CH), 7.68 (t, 2H, ^3J = 7 Hz, ArH), 7.60 (d, 1H, ^3J = 7 Hz, ArH), 7.10 (s, 2H, ArH), 3.95 (s, 3H, OCH_3), 3.84 (s, 6H, 2 × OCH_3). ^{13}C NMR (100 MHz; d_5-pyridine) δ_C, ppm: 156.5, 154.3, 141.6, 140.6, 140.3, 140.0, 139.9, 139.7, 137.8, 132.1, 131.5, 130.3, 130.2, 130.0, 129.9, 129.7, 129.3, 129.1, 129.0, 128.4, 123.4^h, 105.8, 60.8, 56.2, 37.2. MS (MALDI TOF) *m/z*: 821 $[M+H]^+$.

2.2. Photochemical and solvatochromic studies

All measurements were carried out on a Hitachi U-1900 spectrophotometer. All solvents were obtained from commercial suppliers and were used without further purification, with the exception of acetone, ethyl acetate, methanol, ethanol, *n*-hexane, pyridine and dichloromethane, which were distilled prior to measurements. UV–Vis spectra were recorded in the range 300–900 nm.

The photooxidation reaction of 1,3-diphenylisobenzofuran (DPBF) was used to determine singlet molecular oxygen ($^1\Delta_g$) generation by the photosensitizers following lately presented methodologies [22–24]. The kinetics of DPBF photooxidation were studied by observing the decrease of the absorbance at λ_{max} = 417 nm. The efficiency of singlet oxygen generation was measured in DMSO solutions (3.0 mL) (no oxygen bubbled) using the relative method with zinc phthalocyanine (ZnPc, Sigma–Aldrich) as a reference and DPBF as a scavenger for singlet oxygen. Solutions of the sensitizers (absorbance < 0.2 at the irradiation wavelength) ZnPc (0.82×10^{-5} mol/dm^3), **8** (2.45×10^{-5} mol/dm^3), **12** (1.95×10^{-5} mol/dm^3) in DMSO containing DPBF (3.35×10^{-5}, 4.60×10^{-5}, 4.64×10^{-5} mol/dm^3, respectively) were prepared in the dark and irradiated in their Q-band region with light from an ordinary Philips lamp (230 V, 75 W). High-energy wavelengths were filtered out by passing the incident beam through a cut-off Schott KC17 filter (650 nm). The distance between the lamp and the UV–Vis cuvette was 30 cm and the light intensity was set to 8.5 mW/cm^2 (measured by a radiometer RD 0.2/2 with a TD probe, *Optel*). Measurements of the sample and reference under the same conditions enabled quantum yield calculations by direct comparison of the slopes in the linear region of the semi-logarithmic plots of $\ln A_0/A$ vs. irradiation time obtained (in seconds) for the samples and the corresponding slopes obtained for the reference. The singlet oxygen quantum yields $\Phi_{\Delta(\text{sample})} = (k_{\text{sample}}/k_{\text{ZnPc}}) \cdot (A_{\text{ZnPc}}/A_{\text{sample}}) \cdot \Phi_{\Delta(\text{ZnPc})}$, where $\Phi_{\Delta(\text{ZnPc})}$ is the singlet oxygen quantum yield for the reference (ZnPc) in DMSO ($\Phi_{\Delta(\text{ZnPc})} = 0.67$) [25], k_{sample} ($k_{\mathbf{9}} = 0.0005$ s^{-1} and $k_{\mathbf{12}} = 0.0041$ s^{-1}) and k_{ZnPc} (0.0029 s^{-1}) are the DPBF photobleaching rates in the presence of the samples and reference, respectively. A_{ZnPc} and A_{sample} are the absorbances at the Q-band (area under the absorption spectra from 520 to 800 nm) of the samples and the reference, respectively.

2.3. Crystallography

Single crystals of **4** and **6** were obtained at room temperature by slow evaporation of ethyl acetate–*n*-hexane solutions. The structures were solved by direct methods with SHELXS97 and were refined with SHELXL97 by full matrix least-squares based on F^2 [26]. All non-hydrogen atoms were refined anisotropically. All H atoms were generated geometrically, with C–H = 0.93–0.98 Å, and refined as riding on their carriers, with $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$ and $1.5U_{\text{eq}}(C)$ for methyl groups. Details on data collection and refinement, fractional atomic coordinates, anisotropic displacement

parameters, full list of bond lengths and angles in CIF format have been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

3.1. Synthesis

Following the procedure of Tanaka et al. [19], the 1,3-diketones **1a** and **1b** were coupled with ethyl bromoacetate by treatment with NaH in THF to give **2a** and **2b**, respectively (Scheme 1). Subsequent condensation of **2a** with diaminomaleonitrile (**3**), according to the method reported by Begland et al. [27] using oxalic acid in benzene, led to the novel dicyanodiazepine **4**.

X-ray study showed that the 6-substituted dicyanodiazepine ring of **4** has a non-planar molecular structure (Fig. 1). The diazepine ring exhibits a slightly distorted boat conformation with a mirror plane through atom C6 and bisecting bond C2–C3. The dinitrile side of the ring is flattened due to the aromatic character of this part of the ring. Both methyl groups are located on the same side of the ring, opposite to the hydrogen at C6 which is placed axially over the diazepine ring. The other C6-ethoxycarbonylmethyl substituent approaches an equatorial position. Conformational aspects of trisubstituted 1,4-diazepine-2,3-dicarbonitriles have been examined so far for various derivatives differentiated at the C5, C6 and C7 positions, and revealed that their conformation is a consequence of the C6 center chirality and ring atropoisomerism. These compounds typically prefer a conformation in which the C6 substituent (provided it is not a *t*-butyl group) is in the equatorially disposed position [28]. In the solid state **4** is present in the form of the 6*H* tautomer, similarly to the previously obtained diazepine compounds [11]. Unfortunately, condensation of **2b** with **3** using oxalic acid in benzene or P_2O_5 in ethanol did not lead to diazepine product formation (no examples have been found in the literature [29]) and only mono-condensed intermediates were isolated.

Dicyanodiazepine **4** was reduced to the tetrahydrodiazepine **5** using sodium borohydride in methanol, and the latter was dimethylated to **6** using the conditions (NaH, $(CH_3)_2SO_4$ in DMF) reported by Baum and co-workers [15]. An X-ray study showed

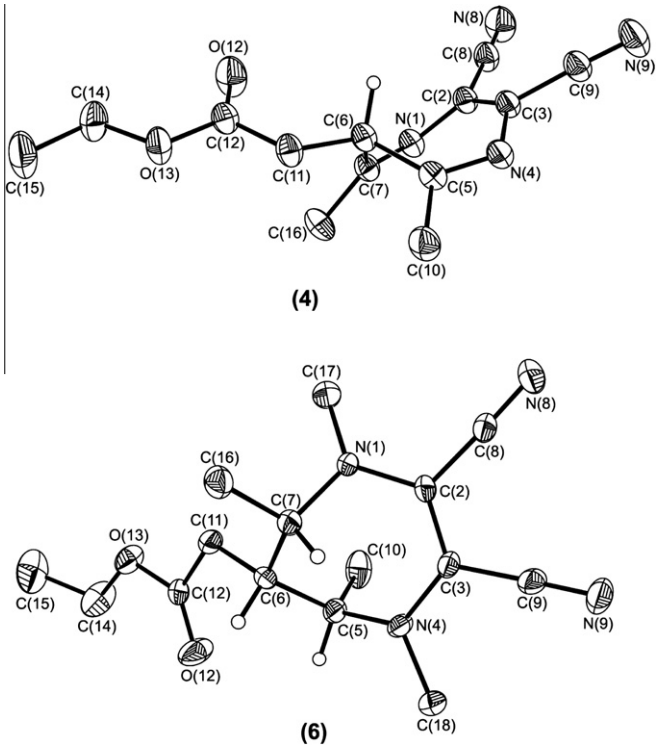
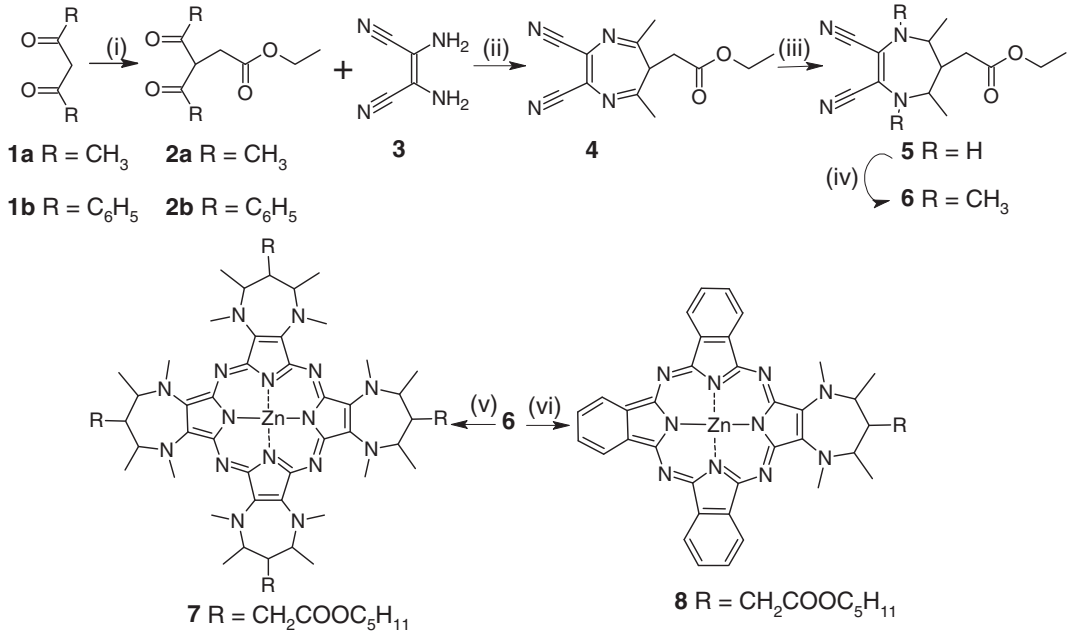


Fig. 1. The molecular structures of **4** and **6** showing the atom-labeling scheme (displacement ellipsoids are shown at the 50% probability level). The methyl and methylene hydrogens are omitted for clarity.

that the dinitrile part (N1, C2, C3, N4) of the ring and C6 are coplanar with C5 and C7, forming up-and-down waves. Interestingly, the configurations at C5 and C7 indicate that this molecule is in fact a *meso* achiral diastereoisomer (Fig. 1). According to the X-ray structures of **4** and **6**, and a ^1H–^1H NOESY NMR study of **5** (Table 1S, Fig 1S, Supplementary data), it seems that the reduction



Scheme 1. *Reagents and conditions*: (i) **2a** [16–18] – NaH, THF, 0 °C, 1 h; next $BrCH_2COOC_2H_5$, rt, 48 h (83%); **2b** [19] – NaH, THF, 0 °C, 1 h; next $BrCH_2COOC_2H_5$, rt, 48 h (74%); (ii) $(CO_2H)_2$ (cat.), benzene, reflux, 41 h (12%); (iii) $NaBH_4$, CH_3OH, −5 °C, 45 min; next rt, 1.5 h (90%); (iv); NaH, DMF, −15 °C, 1 h; next $(CH_3)_2SO_4$, −15 °C, 2 h 15 min (81%); (v) $Zn(OAc)_2$, DBU, *n*PeOH, 130 °C, 16 h (7%); (vi) phthalonitrile, $Zn(OAc)_2$, DBU, *n*PeOH, 130 °C, 24 h (13%).

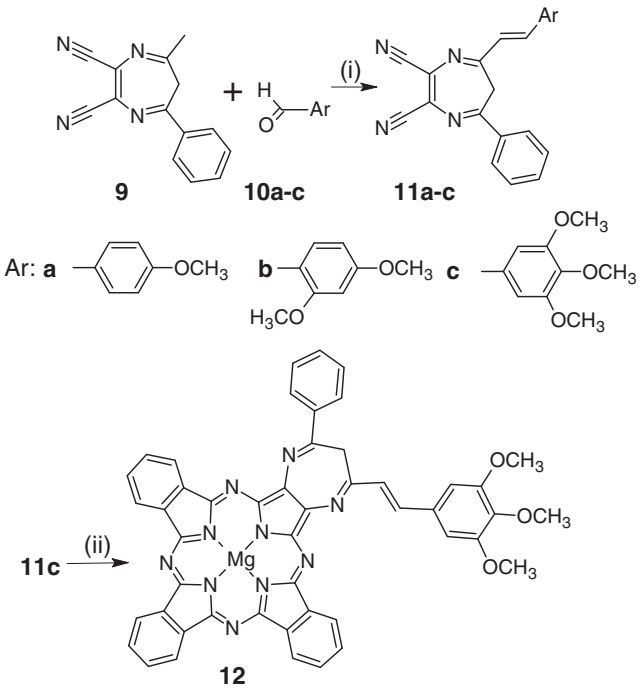
reaction of **4** involves the diastereoselective addition of a hydride to C5 and C7 from the less crowded, concave side of the ring.

Compound **6** was used in a macrocyclization reaction with zinc acetate and DBU in pentanol to give the novel symmetrical porphyrazine **7** in 7% overall yield as a mixture of stereoisomers. Various NMR techniques were found to be useful to fully characterize the structure of **7** (Table 2S, Fig 2S, Supplementary data). Mixed macrocyclization of **6** with a 10-fold excess of phthalonitrile, applying zinc acetate and DBU in pentanol, gave the novel light blue tribenzoporphyrazine **8** in 13% overall yield. Tribenzoporphyrazine **8** was separated from Zn(II)–phthalocyanine by column chromatography on silica using *n*-hexane–ethyl acetate, 7:1 to 7:1.5.

Tribenzoporphyrazine **8** protons present in the α-positions of the annulated benzene rings were observed in the lowest field region at 9.54 and 9.75 ppm, whereas β-protons appeared as a multiplet at 8.18 ppm (Table 3S, Fig. 3S, Supplementary data). Such protons shifts present for benzo-fused rings to the porphyrazine core have been lately explained by a strong deshielding effect of the macrocyclic π-ring current [13]. The ^{1}H–^{1}H COSY spectrum of **8** revealed connectivities in the benzo-fused part, C5–C6–C7 fragment of tetrahydrodiazepine ring and a pentoxy fragment of the pentoxycarbonylmethyl substituent. The ^{1}H–^{1}H NOESY cross-peaks gave information on the spatial orientation of the C5- and C7-methyl groups and C5- and C7-hydrogens, as well as the C6-pentoxycarbonylmethyl group and C6-hydrogen. For the C5- and C7-methyl groups, with a ^{1}H signal at 1.68 ppm, a large nuclear Overhauser effect (NOE) to the neighboring C6–CH_2 protons resonating at 2.92 ppm and N–CH_3 protons resonating at 4.51 ppm was observed. A parallel weak NOE signal was observed between the C6–H proton and C5- and C7-methyl groups, while the C6-H proton showed a large NOE to the neighboring C5- and C7–H protons. Moreover, the C6–CH_2CO protons gave a weak NOE signal to the OCH_2 protons resonating at 4.18 ppm, belonging to the pentoxycarbonylmethyl group. Other NOE effects for N–CH_3 and the adjacent benzo-fused part with ^{1}H signals respectively at 4.51 and 9.54 ppm were observed. The NMR ^{1}H–^{1}H NOESY experiment suggests that the tetrahydrodiazepine tribenzoporphyrazine **8** is a *meso*-diastereoisomer, similar to that observed for the precursor *meso*-dinitrile **6**.

A synthetic study indicated that a direct approach leading to novel diazepinoporphyrazines using diaminomaleonitrile condensation with modified aromatic diketones (like **2b**, Scheme 1) cannot be applied. In order to obtain novel functionalized diazepinoporphyrazines, an attempt was made to check the reactivity of styryldicyanodiazepines in the macrocyclization reaction, which were recently synthesized by Horiguchi and co-workers [21,30,31]. Although styryldicyanodiazepines have been known for 10 years, no attempt, to our knowledge, has been made so far to use them as precursors for the preparation of styryldiazepinoporphyrazines [29].

Firstly, a two-step synthesis of the known dicyanodiazepine **9** was performed by the Horiguchi et al. procedure (Scheme 2) [21]. Condensation reactions of **9** with 4-methoxybenzaldehyde (**10a**), 2,4-dimethoxybenzaldehyde (**10b**) and 3,4,5-trimethoxybenzaldehyde (**10c**) gave the known diazepine **11a** [21] and novel diazepines **11b** and **11c**, respectively. Macrocyclization reaction trials using diazepines **11a**–**11c** revealed that the number and position of the methoxy groups have an influence on the reactivity in the macrocyclization reactions. Diazepine **11c**, containing a trimethoxyphenyl substituent, showed the best reactivity, but under Linstead conditions gave an inseparable mixture of isomers that were difficult to characterize. Consequently, a mixed macrocyclization reaction of diazepine **11c** with a 10-fold excess of phthalonitrile led to the novel styryldiazepinotribenzoporphyrazine **12**, which was successfully separated from Mg(II)-phthalocyanine



Scheme 2. *Reagents and conditions*: (i) **11a** – [21]; **11b** – piperidine (cat.), benzene, reflux, 16 h (41%); **11c** – piperidine (cat.), benzene, reflux, 24 h (64%); (ii) phthalonitrile, Mg(O*n*Bu)$_2$, *n*BuOH, reflux, 21 h (14%).

using silica gel 90 C18-reversed phase for column chromatography with methanol–tetrahydrofurane 10:1.

Tribenzoporphyrazine **12** protons present in the α-positions of the annulated benzene rings were observed in the lowest field region at 9.72 ppm, whereas the β-protons appeared as multiplets at 8.10, 8.16 and 8.21 ppm, which is similar to **8** and corresponds to the literature data [13]. The ^{1}H–^{1}H COSY spectrum of **12** revealed connectivities in the benzo-fused part, vinyl part and C5-phenyl ring. The vinyl part protons belonging to the styryl substituent at C7 resonate at 8.26 and 7.89 ppm with a ^3J value of 16 Hz, very characteristic for *trans*-isomerism present in a styryl moiety (Table 4S, Fig. 4S, Supplementary data). The ^{1}H–^{1}H NOESY cross-peaks gave information on the spatial orientation of the C7 substituted styryl moiety. For the vinyl proton at 8.26 ppm, a large NOE signal to the neighboring protons belonging to the benzo-fused part at 9.72 ppm and a weaker NOE signal to the C5-phenyl group protons at 8.95 ppm were observed. For **12**, no signals attributable to the C6–CH_2 protons of the diazepine ring (CH_2 in 6*H*- or CH and NH in the 1*H*-tautomeric form) were observed. Donzello et al. [13] found out that the rates of the possible tautomerism and/or conformational transformation of the diazepine ring are comparable with the nuclear relaxation time, causing strong line broadening and the disappearance of the resonance signals.

3.2. Solvatochromic effects

The solvatochromic effects of tribenzoporphyrazines **8** and **12** dissolved in a range of protic and aprotic solvents were evaluated by monitoring the changes in the UV–Vis spectra (Fig. 2). The electronic absorption spectra of **8** and **12** revealed a broad intensity Soret band (B-band) in the range 352–365 nm and an intense, broad, diffused or split Q-band in the range 600–750 nm, which resulted from the symmetry reduction of the π-chromophore [13]. The significant intensity of this band is a result of $\pi-\pi^*$ transitions in the macrocyclic system [2,11–13], when going from a symmetrical to a low symmetry porphyrazine. As both tribenzoporphyra-

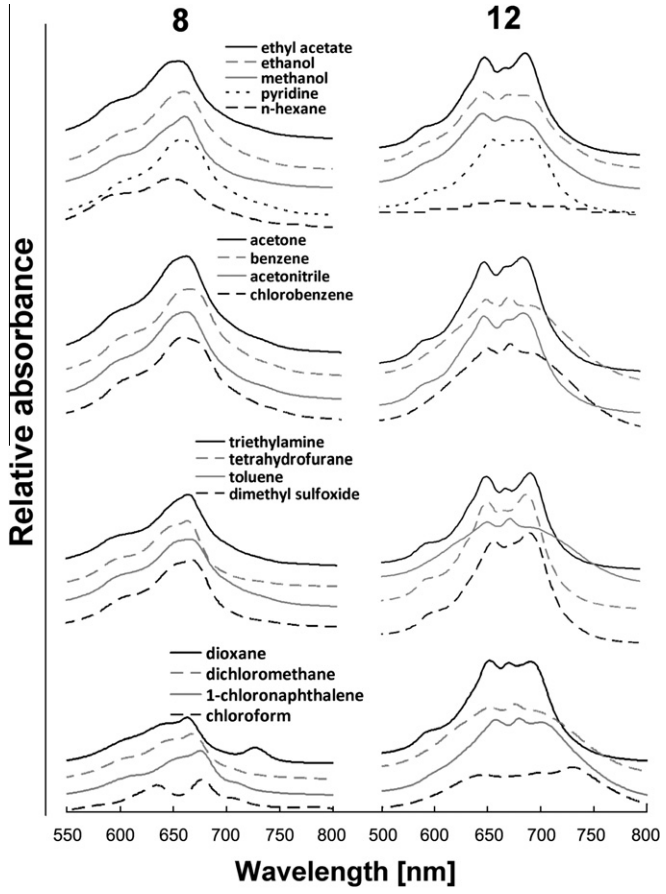


Fig. 2. Normalized UV–Vis spectra of **8** and **12** in different solvents.

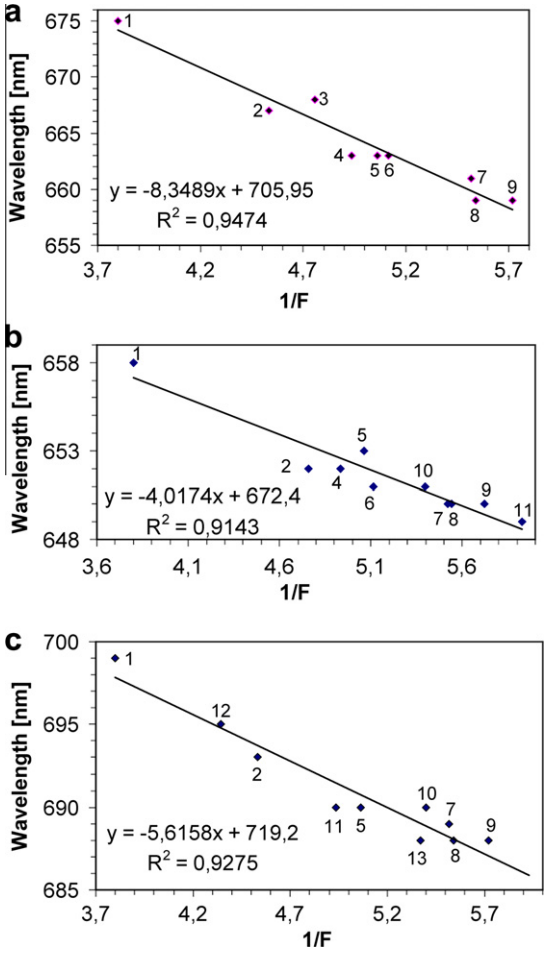


Fig. 3. Plot of the wavelength λ_{max} of the Q-band vs. the refractive index of the solvent described by the rational function $F = (n^2 - 1)/(2n^2 + 1)$ for (a) **8**; (b) **12** (sub-band Q1); (c) **12** (sub-band Q3); where n stands for the refractive index of the solvent: (1) 1-chloronaphthalene, (2) dimethyl sulfoxide, (3) dichloromethane, (4) dioxane, (5) tetrahydrofuran, (6) triethylamine, (7) ethanol, (8) acetone, (9) acetonitrile, (10) ethyl acetate, (11) methanol, (12) pyridine, and (13) *n*-hexane.

zines are unsymmetrical, the Q-band region is relatively broad and may overlap with n–π^* transitions as a result of partial conjugation of N atom lone pairs of the boat-shaped diazepine rings in the 6*H*-form with the central π-chromophore. Broad research performed by Ercolani and Stuzhin [12] on a group of symmetrical diazepine annulated porphyrazines indicated the n–π^* transitions can mix with π–π^* transitions and gain in intensity, appearing in the Q-band. A spectral feature characteristic for diazepinoporphyrazines is an additional sub-band present in the Q-band region.

The positions and intensities of some bands in **8** and **12**, especially the Q-band, were also affected by the type of solvent used and aggregation (Table 5S, Supplementary data). For **8**, the Q-band was present at λ_{max} = 635–677 nm. It was found that the Q-band's red shift was the greatest when chloroform was used as the solvent and an additional Q-band split (635 and 677 nm) was observed. For dioxane, besides the Q-band at 663 nm, an additional band at 727 nm was observed. As follows from Fig. 2, for **12** Q-band components of similar or different intensities, Q1–Q3, were present at λ_{max} = 645–659 nm, 669–699 and 668–729, respectively. The separation of the resulting sub-bands, which is further discussed for Q1 and Q3, strongly depends on the properties of the solvent, which eliminated vibrational structure as the origin of this split. In the UV–Vis spectra of **12**, recorded in ethyl acetate, triethylamine, ethanol, pyridine, benzene, tetrahydrofurane, dioxane, 1-chloronaphthalene and chloroform, the intense Q-band was split into three sub-bands (Q1–Q3). In the UV–Vis spectra of **12** recorded in acetonitrile, acetone and dimethyl sulfoxide, the Q1- and Q3-sub-bands were found, whereas in toluene, chlorobenzene, methanol and dichloromethane, the Q1- and Q2-sub-bands were observed. It was found that the Q-band red shift was greatest when chloroform was used as the solvent. It is noteworthy that the previously obtained tribenzoporhyrazines, possessing an annulated 6*H*-diazepine ring, revealed in the Q-band two well-separated absorptions appearing at 650–660 and 690–700 nm [13].

The correlation between the Q-band shift towards longer wavelengths and the refractive index of the solvent was tested to evaluate the solvatochromic effects [23]. The wavelength corresponding to the maximum of the Q-band, λ_{max}, was plotted against the rational function $F = (n^2 - 1)/(2n^2 + 1)$ of the solvent's refractive index n (Fig. 3), according to known procedures [23,32]. This dependence is linear, even though the influence of the solvent's dielectric constant on the solvatochromic shift is neglected here. Simultaneously, it was checked that for **8** and **12** the Q-band shift was not correlated with the dipole moments (μ) of the solvents tested. A linear correlation for **8** between the Q-band shifts and $1/F$ values with the correlation index R^2 = 0.9474 was found for nine solvents (Fig. 3). A better correlation between the Q-band shifts and $1/F$ values suggests that the solvatochromic effects for **8** are mainly the result of solvation rather than coordination processes [23]. Changes in the UV–Vis spectra of tribenzoporphyrazine **12** and relations between the Q-band shifts (λ_{max}), including Q1- and Q3-sub-bands and $1/F$ values, are shown in Fig. 3 and are presented in Table 5, Supplementary data. It was found that the correlation indices for 10 solvents between Q1- and

Q3-sub-band shifts and $1/F$ values were $R^2 = 0.9143$ and $R^2 = 0.9275$, respectively. Summarizing, the linear nature of the plot suggests that the red shifts in the Q-band are mainly a result of solvation rather than coordination and there is no correlation between the coordinating strength of the solvent and the red shift. A coordinating solvent, such as tetrahydrofuran, gives nearly the same Q-band shift (653 nm) as benzene and dichloromethane (652 nm), confirming that coordination of the solvent does not play a significant role in the red shift.

3.3. Singlet oxygen generation

The potential photosensitizing activity of the obtained novel tribenzoporphyrazines was evaluated by measuring the ability for singlet oxygen production, which is the result of an interaction between an activated photosensitizer and oxygen. DPBF (1,3-diphenylizobenzofuran) was used as a chemical quencher, which undergoes a cycloaddition reaction with singlet oxygen to produce an endoperoxide [22,24,33]. Solutions of DPBF and tribenzoporphyrazines **8** and **12** were irradiated with light above 650 nm. Upon interaction with singlet oxygen, DPBF was oxidized and decomposed, and this was observed in the UV–Vis spectra as a decrease of the absorbance at 417 nm (Fig. 4). This band is a result of DPBF maximum absorption and tribenzoporphyrazine Soret-band overlapping.

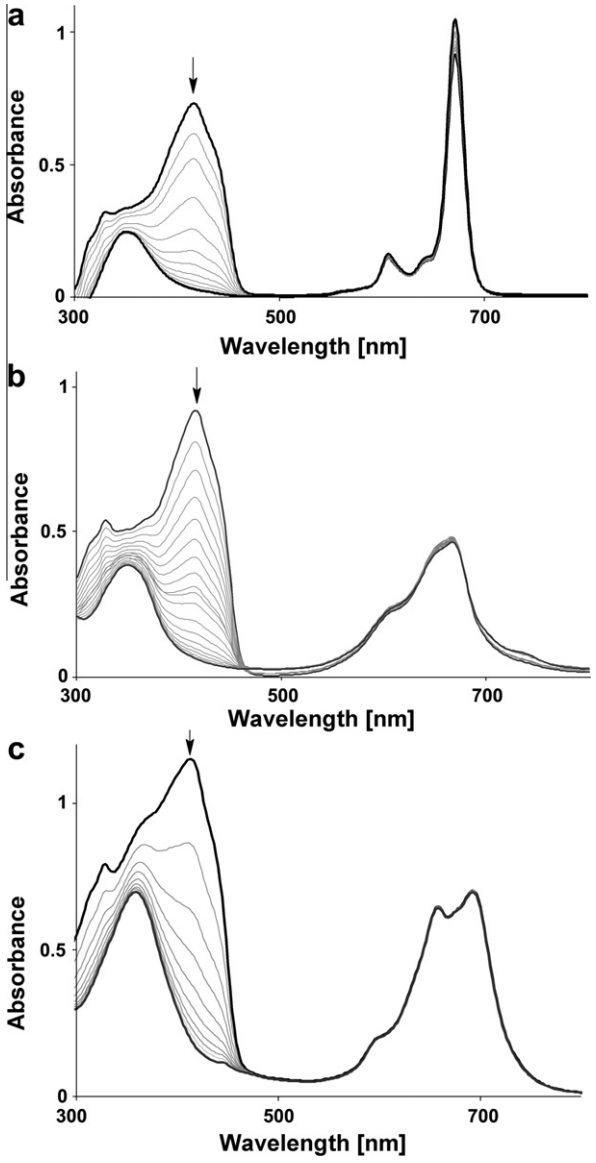


Fig. 4. Changes in the UV–Vis spectra under aerobic conditions in DMSO for: (a) DPBF and ZnPc within 20 min; (b) DPBF and **8** within 104 min; (c) DPBF and **12** within 10 min; ZnPc – zinc phthalocyanine.

The lack of change in the Q-band intensity during irradiation of **12** indicates its good stability and resistance. DPBF was completely oxidized by **12** in 10 min, while the same effect using zinc phthalocyanine (ZnPc) as a reference was reached after 20 min. This experiment shows promising photosensitizing activity for the new tribenzoporphyrazine **12**, which is an efficient singlet oxygen generator with a Φ_Δ value of 0.44, although it is a little lower than that of ZnPc ($\Phi_\Delta = 0.67$ [25]).

Tribenzoporphyrazine **8**, upon singlet oxygen generation measurement, showed a lower activity, with completed oxidation of DPBF after 104 min and a Φ_Δ value of 0.08. A small change in the Q-band intensity of **8** due to phototransformation (a decrease of the Q-band at 667 nm and an increase of the X-band at 730–740 nm) was observed, but this process occurs much slower than the singlet oxygen production. Changes in absorptions of **8** during the 104 min time of this experiment did not exceed 2.1%.

4. Conclusion

Novel tribenzoporphyrazines possessing peripherally annulated tetrahydrodiazepine and diazepine rings were synthesized and characterized. NMR NOESY and X-ray diffraction experiments established that the precursor dinitrile, the tetrahydrodiazepine annulated tribenzoporphyrazine, was obtained as a *meso*-diastereoisomer. A synthetic study indicated that the recently synthesized styryldicyanodiazepines may be treated as precursors for the preparation of tribenzoporphyrazines possessing an annulated styryldiazepine ring.

The novel tribenzoporphyrazines were studied for the substituent effects on their absorption spectra in various solvents and on singlet oxygen generation. Solvatochromic effects of the tribenzoporphyrazines dissolved in a range of protic and aprotic solvents were evaluated by monitoring the changes in the UV–Vis spectra. The correlation between the Q-band shift towards longer wavelengths and the refractive index of the solvent was tested to evaluate the solvatochromic effects. This indicated that the solvatochromic effects for annulated tetrahydrodiazepino- and styryldiazepino-tribenzoporphyrazines are mainly the result of solvation, rather than coordination processes.

The potential photosensitizing activity of the novel tribenzoporphyrazines was evaluated by measuring the ability for singlet oxygen production, which is the result of an interaction between the activated photosensitizer and oxygen. This experiment proves promising photosensitizing activity of the novel styryldiazepinotribenzoporphyrazine, which is an efficient single oxygen generator with a Φ_Δ value of 0.44, although it is a little lower than that of zinc phthalocyanine. Tetrahydrodiazepinotribenzoporphyrazine showed a lower activity for singlet oxygen generation ($\Phi_\Delta = 0.08$). The direction of this research will be continued and reported in due course.

Acknowledgements

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Appendix A. Supplementary data

CCDC 801855 and 801856 contain the supplementary crystallographic data for **4** and **6**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223–336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2010.12.049.

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