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Tetra[6,7]quinoxalinoporphyrazines: The Effect of an Additional Benzene Ring on Photophysical and Photochemical Properties

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Synthetic methods for a series of zinc tetra[6,7]quinoxalinoporphyrazines (6,7-TQP) with peripheral chains connected through the S, O and N heteroatoms as well as through the C–C bond were developed. Photophysical and photochemical properties of 6,7-TQP were compared with tetrapyrazinoporphyrazines (TPP) bearing the same peripheral substituents to disclose the effect of insertion of a benzene ring between the pyrazine and porphyrazine moieties. The influence of the peripheral heteroatom in the group of 6,7-TQP is also discussed. Prepared 6,7-TQP have their main absorption band (Q-band) strongly batho- and hyperchromically shifted (λ_{max} = 730–770 nm in pyridine, ε up to 500000 dm^3 mol^{-1} cm^{-1}) in comparison to TPP. They showed high singlet oxygen quantum yields (Φ_Δ = 0.50–0.74) and relatively low fluorescence quantum yields ($\Phi_F < 0.08$).

Introduction

Phthalocyanine (Pc) and their derivatives have attracted the steady attention of researchers for a long time because of the prospective photophysical and photochemical properties of these compounds. They found their place in many different areas as industrial dyes[1,2] chemical sensors,[3] fluorophors,[4] electrocatalysts[5,6] photosensitizers in photodynamic therapy[7] and antennas in artificial photosynthesis or solar energy conversion.[8,9] Since many of the abovementioned applications are based on excitation by light, the absorption profile of newly prepared Pc chromophores serves often as the first feature to reveal their potential impact for practical use. Light of longer wavelength is less scattered by the environment, allowing the ray of activating light to be aimed at a particular target. At the same time, human tissues are also more permeable to light of longer wavelengths (close to 800 nm), thus allowing a deeper therapeutic hit in, for example, photodynamic therapy. A high extinction coefficient (ε) of the activating wavelength is beneficial, as it ensures the same effect at lower dye concentration. In summary, redshifted absorption and higher ε are considered to be advantageous in many applications.

Pcs have their main absorption band (Q-band) between 670–700 nm with ε usually up to 200000 dm^3 mol^{-1} cm^{-1}. The absorption maximum can be redshifted by suitable peripheral substitution of the Pc ring.[10] However, a more pronounced effect is generally achieved by enlargement of the π-conjugated system.[11,12] Thus, condensation of another aromatic ring to the Pc core can shift the absorption bathochromically, resulting in naphthalocyanines (Ncs) or tetra[6,7]quinoxalinoporphyrazines (6,7-TQPs) if the ring is benzene or pyrazine, respectively. Ncs are well known and widely investigated compounds.[13,14] 6,7-TQPs have been discovered only recently[15,16] because of the lack of reliable synthetic methods leading to their precursors. However, recent developments[17–19] in the synthesis of a key starting material 4,5-diaminophthalonitrile (**1**) will surely lead to more extensive exploration of this class of organic dyes.

All up to now, prepared and investigated 6,7-TQPs have their peripheral chains connected solely through carbon.[20] However, a heteroatom connecting the peripheral chain is known to alter substantially the behaviour of the whole macrocycle.[21] Recently, we developed a synthetic method to alkylamino 6,7-TQP derivatives.[22] In the presented work, we show a synthetic route to the series of 6,7-TQPs bearing peripheral chains connected through the S and O heteroatoms as well as through the C–C bond. To reveal the effect of enlargement of the macrocyclic system on the photophysical and photochemical properties, we compared prepared 6,7-TQPs with their lower homologues from a group of tetrapyrazinoporphyrazines (TPPs) bearing the same substituents.

Results and Discussion

Synthesis

Similarly to Pc and related compounds, the synthesis of the 6,7-TQPs was performed by cyclotetramerization of

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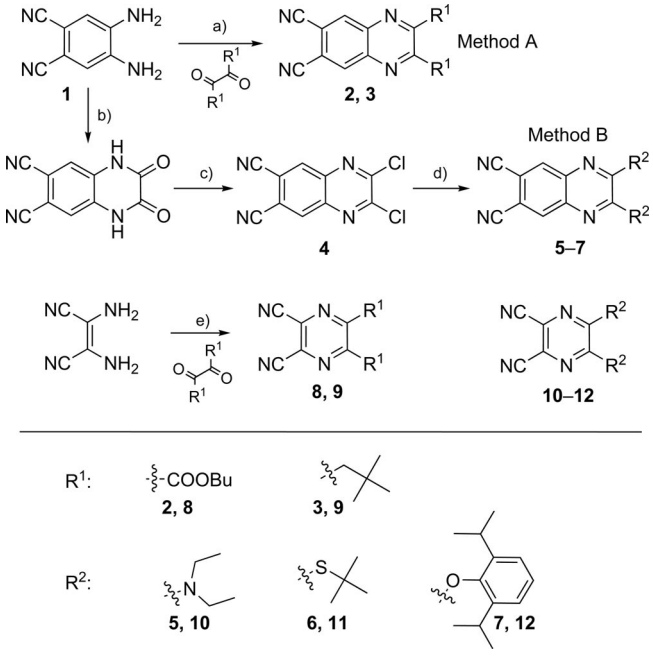
aromatic *ortho*-dicarbonitriles. In this case, suitably 2,3-disubstituted quinoxaline-6,7-dicarbonitriles were prepared. A choice of peripheral substituents was lead by the idea of lowering undesirable aggregation of the final 6,7-TQP macrocycle. Aggregation induces a release of energy by different relaxation channels (usually through heat) that would misrepresent the obtained photophysical and photochemical data. The synthesis of the precursors was carried out via two different approaches (Scheme 1). Compounds **2** and **3** having their substituents connected through the C–C bond were prepared by condensing **1** with appropriately substituted vicinal diketones (Method A) that were prepared similarly to published procedures.[23,24] As the reaction is facilitated in acidic medium, acetic acid was used as the solvent. Method B employing the recently developed intermediate 2,3-dichloroquinoxaline-6,7-dicarbonitrile (**4**) [22] was used for the synthesis of heteroatom-linked peripheral chain bearing precursors **5**–**7**. The chlorine atoms on the electron-deficient positions of **4** are easily exchanged by nucleophilic substitution with amines to compound **5**. Thiolates and phenolates as stronger nucleophiles reacted rapidly with **4** under mild conditions to yield precursors **6** and **7**, respectively, in good yields. Most of the studied TPPs were synthesized by published procedures. That is why only precursor **9** had to be prepared newly by condensation of diaminomaleonitrile with the appropriate diketone by applying method A. Also, a published synthesis of **12**[25] was modified, giving comparable yields (83% this work, 78% published) in much shorter time (15 min instead of 24 h) without the necessity of anhydrous conditions.



Scheme 1. Synthesis of precursors. Reagents and conditions: (a) acetic acid, THF, reflux, 3–9 h; (b) EtOH, diethyl oxalate, 140 °C, 8 h; (c) 1,2-dichloroethane, $SOCl_2$, DMF, reflux, 3 h; (d) for **5**: diethylamine, THF, room temp., overnight; for **6**, 2-methylpropan-2-thiol, NaOH/water, THF, room temp., 15 min; for **7**: 2,6-diisopropylphenol, NaOH/water, THF, room temp., 130 min; (e) acetic acid, reflux, 2–9 h.

Thereafter, the prepared precursors were subjected to a cyclotetramerization reaction. **TPP1**, **TPP3** and **TPP4** were synthesized according to published procedures. The several-step method using cyclization of appropriate precursor (**2**, **3**, **5**, **6** and **9**) via magnesium butoxide initiator followed by demetallation by *p*-toluenesulfonic acid and subsequent chelation of zinc into the centre of the metal-free macrocycle by using anhydrous zinc acetate was revealed as the best approach to **TQP1**–**TQP4** and **TPP2** (Figure 1). Other procedures using lithium butoxide as initiator or employing the template effect of the zinc cation in high boiling solvents (DMF, DMAE, quinoline) did not lead to better results. It is interesting to point out that the magnesium butoxide method was also successful in the preparation of **TQP3**, although our previous attempts did not lead to the desired product.[22]

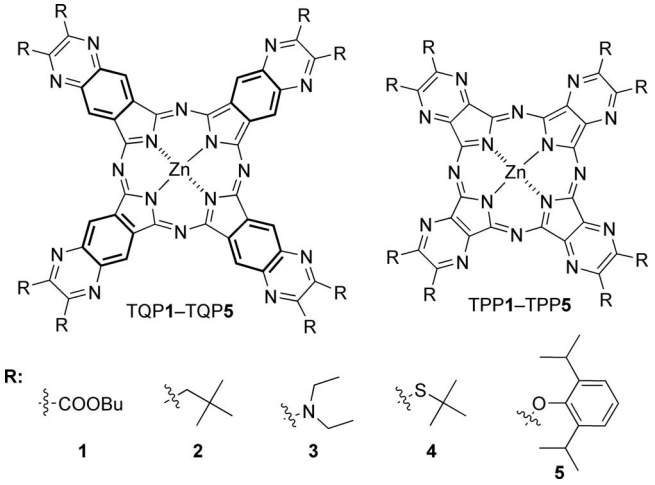


Figure 1. Structures of macrocycles investigated in this work.

The problematic part of the synthesis was **TQP1**, where a major, deep-blue side product sticking to the baseline of the TLC plate (toluene/pyridine, 5:1) was observed aside from the anticipated product (R_f = 0.72). Its appearance was detected even for the Mg complex. A longer reaction time led to a significantly more intense fraction on the start. We isolated both fractions by scraping them from the TLC plate. The mass spectrum (MALDI-TOF) of the fraction with R_f = 0.72 corresponded to desired **MgTQP1** (cluster at m/z = 1544), whereas the mass spectrum of the fraction from the start was composed of clusters at m/z = 1444, 1344, 1244, 1144, etc., corresponding to the stepwise loss of peripheral butoxycarbonyl groups ($\Delta m/z$ = 100). When pure **MgTQP1** was isolated and converted into the zinc complex, similar side products were detected on the start, which were more pronounced when a higher temperature was used during the chelation step. We suggest therefore that a higher temperature may lead to cleavage of peripheral chains, leading to products with stronger aggregation (sticking to the baseline of the TLC plate). As a consequence, we changed

the reaction conditions by shortening the reaction time during tetramerization with Mg butoxide to 3 h and lowering the temperature below 120 °C during chelation step, and under these conditions, **MgTQP1** was obtained with only minor side products.

Cyclotetramerization of aryloxy derivatives of TPP and analogous compounds is known to be complicated by transetherification.[21,26,27] The ether linkages in **7** and **12** are not stable under conditions of the general method described above, as the carbon atoms in the 2- and 3-positions of the quinoxaline (**7**) and in the 5- and 6-positions of the pyrazine ring (**12**) are strongly electron deficient and are attacked by the alkoxide used as the initiator. Recently, Makhseed et al. described a successful method for the cyclotetramerization of **7** into **TPP5** by employing zinc acetate in dry quinoline,[25] but our attempts to repeat their procedure failed. Satisfactory results were achieved with the method developed for similar compounds by Mørkved et al.[28,29] by employing cyclotetramerization of **7** or **12** directly in a melt with a $Zn(quinoline)_2Cl_2$ complex.

Due to the presence of aggregation inhibiting substituents, all prepared compounds showed very good solubility in common laboratory solvents. A peculiar behaviour was observed only for **TQP2**, which was practically insoluble (only slightly in DMF and pyridine) despite its bulky neopentyl substituents. For comparison, its homologue **TPP2** or isoster **TQP4** showed very good solubility.

UV/Vis Absorption

The shapes of the absorption spectra of prepared **TQP1**–**TQP5** were typical for similar macrocycles (TPP, Pc, Nc) with a low-energy Q-band in the area 730–770 nm and a high-energy B-band in the area 320–430 nm (Figure 2). The significant redshift of approximately 100 nm compared to the corresponding TPP is obvious from Table 1. The most manifested redshift ($\Delta\lambda$) occurred between derivatives bearing peripheral substituents linked by a C–C bond. It is noteworthy that the effect induced by enlargement of the π-conjugated system of Pc via condensation of pyrazine rings (6,7-TQP) is lower than in the case of isosteric benzene rings (Nc). While the absorption maximum of **TQP4** lies at 754 nm (pyridine), similar octa(alkylsulfanyl)Nc absorbs at 777 nm (THF).[13] Such a hypsochromic effect of the introduction of nitrogen atoms into the macrocyclic core is in accordance with analogous dependences described between Pc and their aza analogues (TPP).[30]

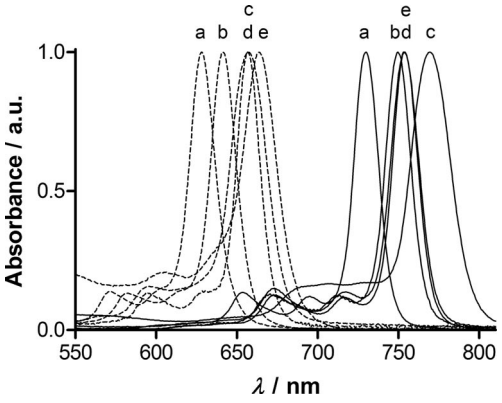


Figure 2. Normalized absorption spectra of TPP (dashed lines) and TQP (solid lines) in pyridine [**1** (c), **2** (b), **3** (e), **4** (d) and **5** (a)].

The position of the Q-band was influenced also by the heteroatom connecting the peripheral chain or by conjugation of the peripheral carbonyl group with the 6,7-TQP π-system (Figure 2, Table 1). Aliphatic alkyls do not contribute to a redshift and compounds with such modification usually absorb at the same wavelength as unsubstituted macrocycles.[31,32] **TQP2** can be therefore considered as the standard for comparison. The butoxycarbonyl groups of **TQP1** shifted the position of the Q-band significantly bathochromically due to the strong conjugation of the carbonyl group with the π-system of the TQP core. The electron-donating *N*,*N*-diethylamine (**TQP3**) and *tert*-butylsulfanyl (**TQP4**) groups also have a positive effect on the bathochromic shift caused by the participation of the lone pair of electrons of the nitrogen and sulfur on the π-system of the macrocycle. However, the effect was only weak (4 nm

Table 1. Photophysical, photochemical and spectroscopic data of the studied compounds in pyridine.

Substitution	Compound	λ_{max} / nm (ε / $dm^3 mol^{-1} cm^{-1}$)	$\Delta\lambda$ / nm	Φ_Δ[a]	Φ_F[a] λ_F / nm	Ref.
C (COOBu)	**TQP1**	770 (247000)	112	0.50	0.015, 780	
	TPP1	658 (158400)		0.52[b]	0.11, 672[b]	[23]
C (neopentyl)	**TQP2**	750 (174000)	108	0.64	0.039, 755	
	TPP2	642 (227400)		0.56	0.24, 648	
N	**TQP3**	754 (223600)	90	0.63	0.032, 760	
	TPP3	664 (183100)		0.020	n.d.[c]	[33]
S	**TQP4**	754 (510000)	97	0.74	0.042, 759	
	TPP4	657 (298000)		0.65	0.30, 663	[33]
O	**TQP5**	730 (411000)	102	0.69	0.075, 735	
	TPP5	628 (200200)		0.61	0.29, 637	

[a] Mean of three independent measurements, estimated error ±15%. No changes in absorption spectra were observed during the measurements. [b] Measured in DMF. [c] Not detected.

when compared to **TQP2**). These heteroatom linkages induced much stronger bathochromic shifts of 22 and 15 nm in their corresponding TPP derivatives **TPP3** and **TPP4**, respectively, when compared to **TPP2**. Conversely to other heteroatom-substituted 6,7-TQP and TPP, aryloxy substitution induced a hypsochromic shift of the Q-band maximum, again more pronounced at the latter type of macrocycles.

As regards a strength of absorption, the 6,7-TQP core has noticeably a positive effect. The TQP core induces 1.3–2.0 times higher ε than corresponding TPP. The only exception is the low value for **TQP2**, which is most likely influenced by its low solubility. In the group of 6,7-TQP, the sulfur- and oxygen-substituted derivatives (**TQP4** and **TQP5**) showed ε values over 400000 $dm^3 mol^{-1} cm^{-1}$, which is approximately two times higher than those connected through carbon or nitrogen (**TQP1**–**TQP3**).

Singlet Oxygen Production and Fluorescence Emission

The efficiency with which the 6,7-TQPs can generate singlet oxygen was evaluated quantitatively by determination of their singlet oxygen quantum yields (Φ_Δ) in pyridine. No changes in the absorption spectra of the 6,7-TQPs were observed during measurements, suggesting that neither photodegradation nor aggregation took place. The results are summarized in Table 1.

All investigated 6,7-TQPs showed high Φ_Δ, indicating very efficient transformation of absorbed light energy into singlet oxygen. Singlet oxygen quantum yields for the corresponding TPP derivatives are lower (except **TQP1**), indicating a positive effect of the 6,7-TQP core on singlet oxygen production. Alkylsulfanyl **TQP4** appeared to be the strongest singlet oxygen producer, confirming similar findings at heteroatom-substituted TPP homologues.[21] As regards alkylamino substitution, quantum yields of singlet oxygen as well as fluorescence quantum yields are extremely low for **TPP3** due to quenching of excited states by intramolecular photoinduced electron transfer.[33] A similar effect was expected for TQP but the enlarged system of **TQP3** showed a Φ_Δ value of 0.63, which is comparable with other 6,7-TQPs in the series, suggesting that photoinduced electron transfer is not a thermodynamically favourable way for the excited state of the macrocycle to relax. For comparison to our data in Table 1, Mitzel et al.[15] described Φ_Δ = 0.56 (THF) for acetylenic zinc 6,7-TQP.

As the absorbed energy is released mainly through singlet oxygen production, the fluorescence quantum yields of all TQPs were relatively low ($\Phi_F < 0.08$, Table 1), generally several times lower than the value for the corresponding TPPs. The shapes of the fluorescence emission spectra were typical for Pcs and related compounds with only small Stokes shift (Figure S3, Supporting Information). The fact that the excitation spectra superimposed the absorption spectra confirmed that the compounds were exclusively in the monomeric form during the measurements of fluorescence as well as singlet oxygen.

Conclusions

In conclusion, heteroatom-substituted 6,7-TQPs benefit from an expanded π-system and the associated batho- and hyperchromically shifted absorption in the Q-band area in comparison to investigated TPP homologues. The enlargement of the macrocyclic core leads to an increase in the values of Φ_Δ and a decrease in the values of Φ_F when compared to the values obtained for the TPP system. As a consequence, TQPs may be useful tools in applications employing singlet oxygen, but not in those based on fluorescence emission. Heteroatom linkage was shown to influence substantially both the photophysical and photochemical properties of the basic macrocyclic core. Due to a strong absorption in the near-infrared region as well as to strong singlet oxygen production, these novel 6,7-TQPs may become an attractive alternative to established porphyrinoid compounds in applications based on absorption of light and singlet oxygen production (e.g., photodynamic therapy, photooxidation, photodegradation of waste waters).

Experimental Section

Materials and Methods: All organic solvents were of analytical grade. Anhydrous butanol was stored over magnesium and distilled prior to use. TLC was performed on Merck aluminium sheets with silica gel 60 F254. Merck Kieselgel 60 (0.040–0.063 mm) was used for column chromatography. The infrared spectra were measured with an IR Spectrometer Nicolet Impact 400 in KBr pellets. The ^1H and ^{13}C NMR spectra were recorded with a Varian Mercury – Vx BB 300 (299.95 MHz for ^1H and 75.43 MHz for ^{13}C). The reported chemical shifts are relative to Me_4Si. Elemental analysis was carried out with an Automatic Microanalyser EA1110CE (Fisons Instruments S.p.A., Milano, Italy). The UV/Vis spectra were recorded by using a UV-2401PC spectrophotometer (Shimadzu Europa, GmbH, Duisburg, Germany). The fluorescence spectra were obtained with an AMINCO-Bowman Series 2 luminescence spectrometer (SLM-Aminco, Urbana, IL, USA). The MALDI-TOF mass spectra were collected with a Voyager-DE STR mass spectrometer (Applied Biosystems, Framingham, MA, USA) calibrated externally with a five-point calibration procedure by using Peptide Calibration Mix1 (LaserBio Labs, Sophia-Antipolis, France). The sample solution (0.5 μL) was spotted onto a target plate, air-dried and covered with 0.5 μL of a matrix solution consisting of 10 μg of α-cyano-4-hydroxycinnamic acid in 100 μL acetonitrile. In the case of **TPP2** and **TQP3**, *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile in DCM (1 mg/500 μL) was used as matrix.

The following compounds were prepared according to literature procedures: **1**,[17] **4**, **5**, **10**,[22] **8** and **TPP1**,[23] **TPP3**,[34] **11** and **TPP4**.[30] 2,2,7,7-Tetramethyloctane-4,5-dione was prepared similarly to a published procedure[24] in 51% yield (yellow oil). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.99 (s, 18 H, CH_3), 2.63 (s, 4 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 29.6, 31.2, 46.8, 200.2 ppm.

Synthesis of Precursors

Dibutyl 6,7-Dicyanoquinoxaline-2,3-dicarboxylate (2): Dibutyl 2,3-dioxosuccinate[23] (326.6 mg, 1.26 mmol) was dissolved in glacial acetic acid (15 mL) and heated to reflux. 4,5-Diaminophthalonitrile (**1**; 200 mg, 1.26 mmol) in THF (5 mL) was added and reflux

was continued for 3 h. The crude product was purified by column chromatography on silica (chloroform) to obtain a pale-yellow solid (242.4 mg, 51%). M.p. 118.1–119.4 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.99 (t, J = 7.4 Hz, 6 H, CH_3), 1.48 (sext., J = 7.5 Hz, 4 H, CH_2CH_3), 1.82 (p, J = 7.1 Hz, 4 H, OCH_2CH_2), 4.50 (t, J = 6.7 Hz, 4 H, OCH_2), 8.72 (s, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 163.35, 147.79, 141.65, 137.30, 116.66, 114.15, 67.45, 30.35, 18.99, 13.63 ppm. IR (KBr): $\tilde{\nu}$ = 3468, 3096, 3067, 3045, 2961, 2937, 2875, 2239 (CN), 1747, 1471, 1435, 1360, 1336, 1279, 1220, 1195, 1135, 1073, 936 cm^{-1}. $C_{20}H_{20}N_4O_4$ (380.40): calcd. C 63.15, H 5.30, N 14.73; found C 63.99, H 5.74, N 14.83.

2,3-Dineopentylquinoxaline-6,7-dicarbonitrile (3): 4,5-Diaminophthalonitrile (**1**; 632 mg, 4 mmol) was added to a stirred solution of 2,2,7,7-tetramethyloctane-4,5-dione (400 mg, 2 mmol) in glacial acetic acid (20 mL), and the mixture was heated at reflux for 9 h. The solvent was evaporated, and the product was purified by column chromatography on silica (chloroform), yielding a white solid (460 mg, 71%). M.p. 154–157 °C (MeOH). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.04 (s, 18 H, CH_3), 3.10 (s, 4 H, CH_2), 8.50 (s, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 161.04, 140.89, 136.66, 115.16, 113.20, 47.54, 34.08, 29.83 ppm. IR (KBr): $\tilde{\nu}$ = 3447, 2965, 2903, 2866, 2240 (CN), 1556, 1473, 1398, 1366, 1335, 1226, 1200, 1131 cm^{-1}. $C_{20}H_{24}N_4$ (320.43): calcd. C 74.97, H 7.55, N 17.48; found C 74.48, H 7.79, N 17.65.

2,3-Bis(*tert*-butylsulfanyl)quinoxaline-6,7-dicarbonitrile (6): 2,3-Dichloroquinoxaline-6,7-dicarbonitrile (**4**; 120 mg, 0.48 mmol) was dissolved in THF (50 mL), and this solution was poured into a solution of 2-methylpropan-2-thiol (104 mg, 1.2 mmol) in 1 M aqueous NaOH (1 mL). This solution was stirred for 15 min at room temperature. The crude product was purified on silica (toluene/chloroform, 4:1) to gain a bright yellow solid (127 mg, 74%). M.p. 219–221 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.72 (s, 18 H, CH_3), 8.25 (s, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 161.82, 139.21, 134.44, 115.39, 112.10, 51.53, 29.74 ppm. IR (KBr): $\tilde{\nu}$ = 3522, 2996, 2964, 2923, 2904, 2864, 2621, 2235 (CN), 1509, 1477, 1456, 1389, 1366, 1360, 1268, 1221, 1166, 1150, 1113, 1030, 899 cm^{-1}. $C_{18}H_{20}N_4S_2$ (356.51): calcd. C 60.64, H 5.65, N 15.72; found C 60.42, H 5.75, N 15.68.

2,3-Bis(2,6-diisopropylphenoxy)quinoxaline-6,7-dicarbonitrile (7): 2,6-Diisopropylphenol (890 mg, 5 mmol) was added to 1 M aqueous NaOH (5 mL), and the mixture was stirred for 40 min at room temperature. This solution was then dropped portionwise into a THF (100 mL) suspension of 2,3-dichloroquinoxaline-6,7-dicarbonitrile (**4**; 470 mg, 1.9 mmol). The mixture was stirred at room temperature for 70 min and THF was then evaporated. The suspension was diluted with water and filtered. Crude product was purified by column chromatography on silica (toluene) and recrystallized from MeOH, yielding a white solid (570 mg, 56%). M.p. 248.5–249.0 °C (MeOH). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.23 (br. s, 24 H, CH_3), 2.97 (sept., J = 6.7 Hz, 8 H, CH_3CHCH_3), 7.29–7.41 (m, 6 H, ArH), 8.08 (s, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 151.67, 146.76, 140.13, 139.70, 133.37, 127.25, 124.46, 115.12, 112.36, 27.98, 23.55 ppm. IR (KBr): $\tilde{\nu}$ = 3474, 2965, 2930, 2870, 2238 (CN), 1617, 1588, 1567, 1502, 1456, 1393, 1363, 1346, 1330, 1252, 1230, 1211, 1173, 1157, 1144, 1092, 1062 cm^{-1}. $C_{34}H_{36}N_4O_2$ (532.68): calcd. C 76.66, H 6.81, N 10.52; found C 76.44, H 7.06, N 10.57.

5,6-Dineopentylpyrazine-2,3-dicarbonitrile (9): 2,3-Diaminomaleonitrile (848 mg, 8 mmol) was added to a stirred solution of 2,2,7,7-tetramethyloctane-4,5-dione (400 mg, 2 mmol) in glacial acetic acid (20 mL), and the mixture was heated at reflux for 9 h. The solvent was evaporated under reduced pressure, and the residue was extracted with chloroform and purified by column chromatography on silica (toluene), yielding a colourless oil that solidified after a while (200 mg, 37%). M.p. 96–97 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.01 (s, 18 H, CH_3), 3.09 (s, 4 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 159.79, 129.51, 113.31, 46.89, 34.08, 29.69 ppm. IR (KBr): $\tilde{\nu}$ = 3478, 2961, 2904, 2869, 2241, 1524, 1472, 1430, 1396, 1378, 1320, 1229, 1199, 1129, 851, 670 cm^{-1}. $C_{16}H_{22}N_4$ (270.37): calcd. C 71.08, H 8.20, N 20.72; found C 71.03, H 8.64, N 20.51.

5,6-Bis(2,6-diisopropylphenoxy)pyrazine-2,3-dicarbonitrile (12): 2,6-Diisopropylphenol (446 mg, 2.5 mmol) was stirred for 15 min at room temperature in 1 M aqueous NaOH (2.4 mL, 2.4 mmol). 5,6-Dichloropyrazine-2,3-dicarbonitrile[35] (200 mg, 1 mmol) in THF (15 mL) was added dropwise, and the mixture was stirred for 15 min at room temperature. The crude product was concentrated to dryness, and the brownish-yellow solid was washed thoroughly with water and purified by column chromatography on silica (toluene/hexane, 1:1), yielding a white solid (404 mg, 83%). M.p. 208.5–209.5 °C (MeOH) {ref.[25] m.p. 253 °C (*n*-hexane)}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.39–7.24 (m, 6 H, aromH), 2.82 (sept., J = 7 Hz, 4 H, CH), 1.23 (d, J = 7 Hz, 24 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 23.2, 28.0, 112.6, 124.2, 124.6, 127.6, 139.8, 146.3, 151.1 ppm. IR (KBr): $\tilde{\nu}$ = 3068, 3032, 2967, 2930, 2871, 2360, 2344, 2237, 1545, 1460, 1441, 1403, 1385, 1357, 1331, 1258, 1233, 1142, 1112, 1089, 1062, 937, 849, 793, 750 cm^{-1}. $C_{30}H_{34}N_4O$ (482.62): calcd. C 74.66, H 7.10, N 11.61; found C 74.40, H 7.31, N 11.99.

General Procedure for the Synthesis of Zinc(II) Tetra[6,7]quinoxalinoporphyrazines TQP1–4: Magnesium turnings and a small crystal of iodine were heated at reflux for 3 h in anhydrous butanol. The appropriate precursor (**2**, **3**, **5** or **6**) was added, and the reaction mixture was heated at reflux for 3 h (**TQP1** and **TQP2**) or 6 h (**TQP3** and **TQP4**). The mixture was left to cool down, and it was then poured into water/methanol/acetic acid 5:5:1 (6:3:1 in the case of **TQP4**) (30–100 mL) and stirred for 30 min at room temperature. The precipitate (**MgTQP**) was collected. Purification of crude **MgTQP** and demetallation to metal-free TQP is mentioned at each compound preparation. Thereafter, metal-free TQP was dissolved in pyridine, anhydrous zinc acetate in DMF was added and the reaction mixture was heated at reflux for 2 h (6 h in the case of **TQP4**). The mixture was concentrated under reduced pressure and water was added. The solid was collected and purified by column chromatography on silica (except **TQP2** and **TQP4**). Mobile phases are mentioned bellow.

2,3,11,12,20,21,29,30-Octakis(butoxycarbonyl)tetra[6,7]quinoxalinoporphyrazine Zinc(II) (TQP1): This compound was prepared according to general procedure mentioned above by using magnesium (112 mg, 5.52 mmol) and compound **2** (250 mg, 0.79 mmol). **MgTQP1** was purified by column chromatography on silica (toluene/pyridine, 10:2) to obtain the Mg intermediate (93 mg, 0.060 mmol). This intermediate was dissolved in chloroform (15 mL) and *p*-toluenesulfonic acid (180 mg, 1.05 mmol) in THF (5 mL) was added; the solution was stirred for 45 min at room temperature. The solvents were evaporated, and the product was thoroughly washed with water and acetone. Metallation was performed according to the general procedure with metal-free TQP (47 mg, 0.031 mmol) and anhydrous zinc acetate (86 mg, 0.47 mmol). Mobile phase toluene/pyridine, 5:1. Blue solid (41 mg, overall yield 16%). ^{1}H NMR (300 MHz, $CDCl_3$/[D_5]pyridine, 25 °C): δ = 0.70 (br. s, 24 H, CH_3), 1.26 (br. s, 16 H, CH_2CH_3), 1.59 (br. s, 16 H, OCH_2CH_2), 4.28 (br. s, 16 H, OCH_2), 9.01 (br. s, 8 H, ArH) ppm.

^{13}C NMR (75 MHz, $CDCl_3$/[D_5]pyridine, 25 °C): δ = 163.74, 151.00, 143.71, 139.63, 137.87, 65.66, 29.73, 18.73, 12.91 ppm. IR (KBr): $\tilde{\nu}$ = 3448, 2959, 2930, 2873, 1726, 1450, 1401, 1374, 1286, 1223, 1159, 1137, 1067, 1035 cm^{-1}. UV/Vis (pyridine): λ (ε, $dm^3 mol^{-1} cm^{-1}$) = 770 (247000), 729 (42300), 698 (39700), 367 (96800), 324 (95100) nm. MS (MALDI-TOF): *m*/*z* = 1585 $[M]^+$. $C_{80}H_{80}N_{16}O_{16}Zn{\cdot}3H_2O$ (1587.00 + 3×18.01): calcd. C 58.55, H 5.3, N 13.66; found C 58.49, H 5.2, N 13.61.

2,3,11,12,20,21,29,30-Octa(neopentyl)tetra[6,7]quinoxalinoporphyrazine Zinc(II) (TQP2): This compound was prepared according to general procedure mentioned above by using magnesium (30 mg, 1.4 mmol) and compound **3** (65 mg, 0.2 mmol). **MgTQP2** precipitated from the solvent during cyclotetramerization and was collected by filtration, washed thoroughly with water, methanol and dichloromethane and recrystallized from hot DMF. Purple needles were collected and washed with DMF and ethanol, yielding 16 mg of a purple solid of magnesium complex. This intermediate (16 mg, 0.012 mmol) was suspended in DMF and heated at 180 °C and *p*-toluenesulfonic acid (50 mg, 0.26 mmol) in DMF (2 mL) was added. After 10 min of heating, the solution was left to cool down, diluted with water (10 mL) and stirred for 30 min at room temperature. The green precipitate (metal free TQP) was collected and washed with water and methanol. Metallation was performed according to the general procedure with metal-free TQP (15 mg, 0.012 mmol) and zinc acetate (50 mg, 0.27 mmol). The solution was concentrated under reduced pressure, diluted with water and the blue precipitate was collected and recrystallized from hot DMF, yielding a blue solid (11 mg, overall yield 16%). IR (KBr): $\tilde{\nu}$ = 3420, 2954, 2904, 2966, 1654, 1474, 1449, 1380, 1365, 1329, 1305, 1230, 1190, 1149, 1083, 1047, 1025, 896 cm^{-1}. UV/Vis (pyridine): λ (ε, $dm^3 mol^{-1} cm^{-1}$) = 750 (173800), 712 (20800), 671 (22500), 365 (56600) nm. MS (MALDI-TOF): *m*/*z* = 1345 $[M]^+$. $C_{80}H_{96}N_{16}Zn{\cdot}3H_2O$ (1347.14 + 3×18.01): calcd. C 68.57, H 7.30, N 15.99; found C 68.61, H 7.20, N 16.03. The solubility of **TQP2** was not sufficient for NMR analyses.

2,3,11,12,20,21,29,30-Octakis(diethylamino)tetra[6,7]quinoxalinoporphyrazine Zinc(II) (TQP3): This compound was prepared according to the general procedure mentioned above by using magnesium (10 mg, 0.43 mmol) and compound **5** (20 mg, 0.062 mmol). **MgTQP3** was sufficiently pure for further reaction; thus, it was dissolved in chloroform (10 mL), trifluoroacetic acid (205 mg, 1.8 mmol) was added and the solution was stirred for 3 h at room temperature. The solvent was evaporated, and the product was thoroughly washed with water. Metallation was performed according to the general procedure with metal-free TQP (7 mg, 5.4 μmol) and anhydrous zinc acetate (7 mg, 0.04 mmol). Mobile phase toluene/pyridine, 10:1. Brown-green solid (3 mg, overall yield 14%). ^{1}H NMR (300 MHz, $CDCl_3$/[D_5]pyridine, 25 °C): δ = 9.45 (br. s, 8 H, ArH), 3.40 (q, *J* = 7 Hz, 32 H, NCH_2), 0.86 (t, *J* = 7 Hz, 48 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$/[D_5]pyridine, 25 °C): δ = 11.9, 42.1, 118.7, 120.6, 138.1, 147.4, 153.0 ppm. IR (KBr): $\tilde{\nu}$ = 2960, 2922, 2852, 1757, 1713, 1541, 1426, 1338, 1286, 1247, 1158, 1141, 1118, 1090, 1023 cm^{-1}. MS (MALDI-TOF): *m*/*z* = 1352 $[M]^+$. UV/Vis (pyridine): λ (ε, $dm^3 mol^{-1} cm^{-1}$) = 754 (223600), 718 (30700), 673 (33700), 387 (115300) nm.

2,3,11,12,20,21,29,30-Octakis(*tert*-butylsulfanyl)tetra[6,7]quinoxalinoporphyrazine zinc(II) (TQP4): This compound was prepared according to the general procedure mentioned above by using magnesium (95.3 mg, 3.92 mmol) and compound **6** (200 mg, 0.56 mmol). **MgTQP4** was collected and washed thoroughly with water and methanol. The crude product was adsorbed to silica, washed thoroughly on a glass frit with methanol, dried and then purified by column chromatography on silica (chloroform/pyridine, 10:1) to obtain a dark-green solid. **MgTQP4** was dissolved in chloroform (15 mL), *p*-toluenesulfonic acid (160 mg, 0.9 mmol) in THF (3 mL) was added and the solution was stirred for 45 min at room temperature. Insoluble light-green solid (metal-free TQP) was collected and washed thoroughly with various solvents (chloroform, toluene, tetrahydrofuran, diethyl ether, hexane, ethanol, water, methanol, ethyl acetate and pyridine). Metallation was performed according to the general procedure with metal-free TQP (86 mg, 0.06 mmol) and anhydrous zinc acetate (570 mg, 3.1 mmol). The crude product was washed thoroughly with water, methanol and hexane, yielding a dark green solid (33 mg, overall yield 16%). ^{1}H NMR (300 MHz, $CDCl_3$/[D_5]pyridine, 25 °C): δ = 1.96 (br. s, 72 H, CH_3), 9.61 (s, 8 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$/[D_5]pyridine, 25 °C): δ = 156.62, 153.48, 139.11, 136.74, 121.36, 50.40, 30.26 ppm. IR (KBr): $\tilde{\nu}$ = 3447, 2961, 2920, 2860, 2361, 1719, 1516, 1457, 1362, 1337, 1252, 1123, 1018, 892 cm^{-1}. UV/Vis (pyridine): λ (ε, $dm^3 mol^{-1} cm^{-1}$) = 754 (509800), 717 (60000), 674 (64200), 383 (183200) nm. MS (MALDI-TOF): *m*/*z* = 1488 $[M]^+$, 1432 $[M - C_4H_9]^+$, 1376 $[M - 2C_4H_9]^+$, 1320 $[M - 3C_4H_9]^+$, 1264 $[M - 4C_4H_9]^+$. $C_{72}H_{80}N_{16}S_8Zn{\cdot}3H_2O$ (1491.44 + 3×18.01): calcd. C 55.95, H 5.6, N 14.50; found C 55.79, H 5.7, N 14.45.

2,3,11,12,20,21,29,30-Octakis(2,6-diisopropylphenoxy)tetra[6,7]quinoxalinoporphyrazine Zinc(II) (TQP5): Precursor **7** (500 mg, 0.94 mmol) and $Zn(quinoline)_2Cl_2$ (370 mg, 0.94 mmol, prepared according to the literature[28]) were mixed and heated at 310 °C under an atmosphere of argon for 1 h. The product was washed with methanol/water/acetic acid (5:5:1) and purified by column chromatography on silica (toluene/hexane/pyridine, 100:30:1). Isolated product was washed with methanol, yielding a pale green solid (120 mg, 23%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.45 (s, 96 H, CH_3), 3.63 (sept., *J* = 6.8 Hz, 16 H, CH_3CHCH_3), 7.48–7.58 (m, 24 H, ArH), 9.88 (s, 8 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 153.78, 148.24, 141.36, 139.30, 137.58, 127.74, 125.32, 121.37, 28.54, 24.00, 23.19 ppm. IR (KBr): $\tilde{\nu}$ = 3433, 2964, 2930, 2870, 1421, 1324, 1229, 1183, 1164, 1145, 1092, 1041 cm^{-1}. UV/Vis (pyridine): λ (ε, $dm^3 mol^{-1} cm^{-1}$) = 730 (410800), 695 (49800), 654 (55800), 371 (148200), 322 (76400) nm. MS (MALDI-TOF): *m*/*z* = 2193 $[M]^+$. $C_{136}H_{144}N_{16}O_8Zn{\cdot}3H_2O$ (2196.11 + 3×18.01): calcd. C 72.59, H 6.7, N 9.96; found C 72.63, H 6.7, N 10.05.

Synthesis of Zinc(II) Tetrapyrazinoporphyrazines (TPP)

2,3,9,10,16,17,23,24-Octakis(neopentyl)-1,4,8,11,15,18,22,25-(octaaza)phthalocyanine Zinc(II) (TPP2): Magnesium turnings (24 mg, 1.0 mmol) and a small crystal of iodine were heated at reflux for 3 h in anhydrous butanol (10 mL). Compound **9** (38 mg, 0.14 mmol) was added, and the reaction mixture was heated at reflux for 14 h. The mixture was left to cool down, poured into 50% (v/v) acetic acid (100 mL) and stirred for 30 min at room temperature. The precipitate was collected, washed with 5% v/v $NaHCO_3$, water and methanol to obtain 35 mg of magnesium complex of TPP. This intermediate was stirred in THF (15 mL) with *p*-toluenesulfonic acid (52 mg) for 4 h at room temperature. The solvent was evaporated, and the product was thoroughly washed with water. This metal-free TPP (30 mg) was then dissolved in chloroform, anhydrous zinc acetate (51 mg) in DMF was added, and the mixture was heated at reflux for 4 h. The mixture was concentrated and water was added. A blue solid was collected, washed with water and methanol and purified by column chromatography on silica (chloroform/ethyl acetate, 20:3) to obtain a blue solid (24 mg, 60%). ^{1}H NMR (300 MHz, pyridine, 25 °C): δ = 1.25 (s, 72 H, CH_3), 3.65 (s, 16 H, CH_2) ppm. ^{13}C NMR (75 MHz, pyridine,

25 °C): δ = 157.53, 152.32, 148.38, 48.03, 34.36, 30.24 ppm. IR (KBr): $\tilde{\nu}$ = 2949, 2927, 2857, 1734, 1636, 1549, 1496, 1459, 1359, 1346, 1278, 1238, 1195, 1139, 1093, 1045, 1024 cm^{-1}. UV/Vis (pyridine): λ (ε, $dm^3 mol^{-1} cm^{-1}$) = 642 (227400), 583 (30200), 356 (111800) nm. MS (MALDI-TOF): *m*/*z* = 1144 $[M]^+$. $C_{64}H_{88}N_{16}Zn$ (1146.90): calcd. C 64.98, H 7.84, N 18.95; found C 65.38, H 8.16, N 17.56.

2,3,9,10,16,17,23,24-Octakis(diethylamino)-1,4,8,11,15,18,22,25-(octaaza)phthalocyanine Zinc(II) (TPP3): This compound was prepared according to the published procedure.[34] UV/Vis (pyridine): λ (ε, $dm^3 mol^{-1} cm^{-1}$) = 664 (183100), 604 (36400), 521 (39800), 385 (138600) nm.

2,3,9,10,16,17,23,24-Octakis(2,6-diisopropylphenoxy)-1,4,8,11,15,18,22,25-(octaaza)phthalocyanine Zinc(II) (TPP5): $Zn(quinoline)_2Cl_2$ (246 mg, 0.6 mmol, prepared according to the literature[28]) and **12** (300 mg, 0.6 mmol) were mixed and heated at 260 °C under reflux for 90 min. The product was washed thoroughly with methanol/water (1:1) and purified by column chromatography on silica (toluene/chloroform/THF/pyridine, 15:15:1:1) to obtain a green solid (85 mg, 27%). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.58 (t, *J* = 7 Hz, 8 H, aromH), 7.45 (d, *J* = 8 Hz, 16 H, aromH), 3.32 (sept., *J* = 7 Hz, 16 H, CH), 1.30 (d, *J* = 7 Hz, 96 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 23.5, 28.1, 124.4, 126.6, 141.0, 142.4, 147.9, 149.7, 151.5 ppm. IR (KBr): $\tilde{\nu}$ = 3065, 1965, 2931, 2870, 1541, 1401, 1294, 1249, 1213, 1161, 1145, 1094, 1059, 929 cm^{-1}. UV/Vis (pyridine): λ (ε, $dm^3 mol^{-1} cm^{-1}$) = 628 (200200), 571 (27700), 372 (117600) nm. MS (MALDI-TOF): *m*/*z* = 1993 $[M + H]^+$. $C_{120}H_{136}N_{16}O_8Zn \cdot 5H_2O$ (1995.88 + 5×18.01): calcd. C 68.50, H 7.09, N 10.65; found C 68.55, H 6.13, N 10.78.

Singlet Oxygen and Fluorescence Quantum Yields: Quantum yields of singlet oxygen formation (Φ_Δ) were determined in pyridine according to a previously published procedure[36] using the decomposition of 1,3-diphenylisobenzofuran (DPBF). Zinc phthalocyanine (ZnPc) was used as a reference (Φ_Δ = 0.61 in pyridine[37]). Absorption of the dyes in the Q-band area was set approximately to 0.1.

Fluorescence quantum yields (Φ_F) were determined in pyridine by the comparative method using ZnPc as a reference (Φ_F = 0.20 in pyridine[37]). Absorption of the dyes in the Q-band was always below 0.05. The fluorescence quantum yields were calculated according to Equation (1).

$$\Phi_F^S = \Phi_F^R \left(\frac{F^S}{F^R} \right) \left(\frac{1-10^{-A^R}}{1-10^{-A^S}} \right) \quad (1)$$

where *F* is the integrated area under the emission spectrum, *A* is absorbance at excitation wavelength. Superscripts *R* and *S* correspond to the reference and sample, respectively. Excitation wavelength was 370 nm.

Supporting Information (see footnote on the first page of this article): Additional absorption, fluorescence emission and fluorescence excitation spectra.

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