Available online at www.sciencedirect.com
SCIENCE DIRECT®
Tetrahedron Letters
Tetrahedron Letters 45 (2004) 3363–3367

The *meso*–β-linkage as structural motif in porphyrin-based donor–acceptor compounds

Mathias O. Senge,[a,*] Beatrice Rößler,[b] Jörg von Gersdorff,[b] Andreas Schäfer[b] and Harry Kurreck[b]

[a]*Institut für Chemie, Universität Potsdam, Karl-Liebknecht-Str. 24-25, D-14476 Golm, Germany*
[b]*Institut für Chemie, Freie Universität Berlin, Takustr. 3, D-14195 Berlin, Germany*

Received 13 February 2004; revised 21 February 2004; accepted 5 March 2004

Abstract—Synthetic strategies for using the *meso*–β-linkage as a structural motif in electron transfer mimics have been tested. Exploratory syntheses of directly *meso*–β-linked bis- and trisporphyrins and the first representative X-ray structure of a *meso*–β-linked bisporphyrins are reported. The structure reveals a unique form of intramolecular π–π stabilization between one porphyrin and a *meso*-aryl substituent in a second porphyrin unit that accounts for the stability of different atropisomers in trimers. Using β-formyl porphyrins, dipyrromethanes, and suitable quinone precursor aldehydes, mixed condensations gave convenient access to porphyrin–porphyrin–quinone (P–P–Q) donor–acceptor systems consisting of a *meso*–β-linked bisporphyrin, a spacer, and a quinone acceptor.

Covalently linked porphyrin–quinone compounds serve as versatile model compounds for mimicking natural electron transfer (ET) processes.[1] A significant body of information is available on the interrelationship of structure, energetics, spatial orientation, donor–acceptor separation, and substituent effects in ET models. It has also been shown that the relative ordering of the a_{1u} and a_{2u} HOMOs can be modulated significantly by the type of *meso* substituents and the type of porphyrin–porphyrin linkage.[2] Thus, a detailed understanding of the '*interplay of orbital tuning and linker location in controlling electronic communication*'[3] is necessary for both designing novel photonics devices and understanding natural ET processes.

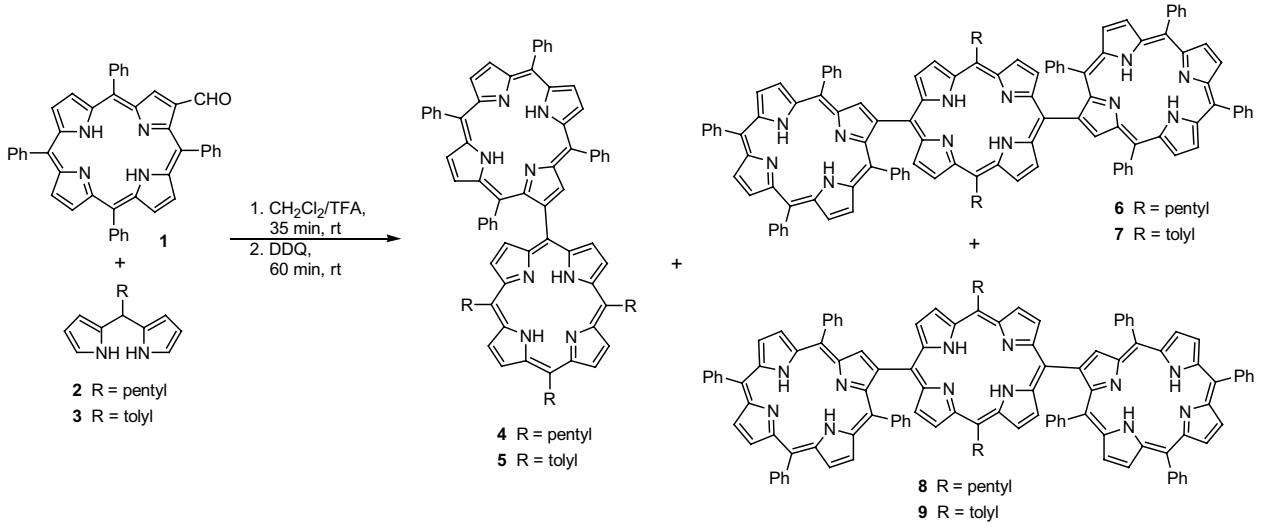
In order to mimic the natural photosynthetic reaction center with its 'special pair' more closely, and to create systems with large charge-separation lifetimes, much attention has focused on using porphyrin dimers as building blocks in ET models. Of special interest are those bisporphyrins where a direct covalent linkage exists between the two porphyrin units. For these, three different types of covalent linkages are possible: *meso*–*meso*,[4,5] β–β,[6] and *meso*–β.[5,7,8] While the advent of Osuka's electrochemical coupling method[2] has greatly facilitated the synthesis of *meso*–*meso*-linked systems, only few examples are known for the latter two, a notable exception for the *meso*–β systems being Wasielewski's phytochlorin derivatives.[7a]

Thus, we have started a project aimed at the evaluation and use of synthetic methods for the rapid construction of electron transfer compounds consisting of directly *meso*–β-linked bisporphyrins and quinone acceptors. In order to gain access to a series of compounds for investigating the interplay of frontier orbital properties and type of porphyrin connection, we chose tetra-*meso* substituted porphyrins and *meso* substituted dipyrromethanes as easily accessible starting materials for condensation reactions. Variation of the *meso* substituents in both components will then allow simple modulation of the electronic and conformational properties of both porphyrin units.

An initial study on the synthetic utility involved acid-catalyzed condensation of 2 equiv of **1** with 2 equiv of *meso* substituted dipyrromethanes,[9a] followed by oxidation with DDQ. BF_3 gave unsatisfactory reactions and thus TFA was used as acid catalyst. Thus, reaction of **1** with **2** gave three products; the dimer **4** (10%) and

Keywords: Electron transfer; Tetrapyrroles; Porphyrin-quinones, porphyrins; Condensation reactions.
* Corresponding author. Tel.: +49-331-977-5187; fax: +49-331-977-5059; e-mail: mosenge@chem.uni-potsdam.de

0040-4039/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2004.03.027



Scheme 1. Exploratory syntheses of bis- and trisporphyrins.

two fractions **6** (5%) and **8** (5%) of trimers.[10] Reaction of **1** with **3** gave similar results (**5** 9%, **7** 5%, **9** 4%). Formation of the dimer is due to acid-catalyzed scrambling of the dipyrromethanes under the reaction conditions used.[12] The two trimers were identified on the basis of NMR (^{1}H, ^{1}H–^{1}H-COSY, NOE) as two atropisomers arising from restricted rotation about the *meso*–β bond (Scheme 1).[7b]

For both *meso–meso*- and β–β-linked bisporphyrins an almost orthogonal orientation of the two porphyrins has been shown in crystal structures.[4a,5,6] In conjunction with the unique spectroscopic properties of bisporphyrins, the degree of dihedral angle twisting is important in controlling the photophysical properties.[13] In order to unambiguously determine the conformation of *meso*–β-linked bisporphyrins a single crystal structure determination of **5** was undertaken (Fig. 1).[14]

The molecular structure in the crystal reveals two distinct features. First, as indicated by the split Soret band (see below), the two porphyrins are tilted against each other into an almost orthogonal orientation. The tilt angle of the two 4N-planes against each other is 106.0°.

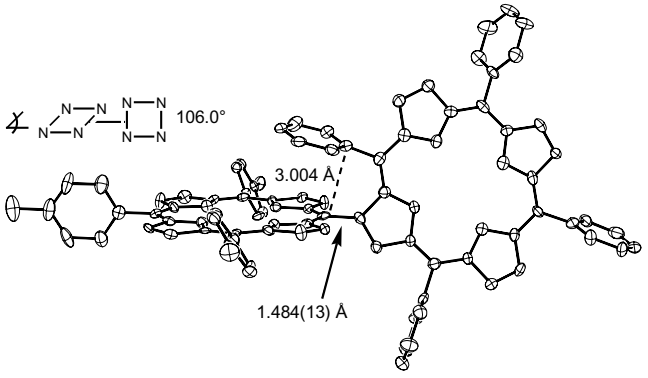
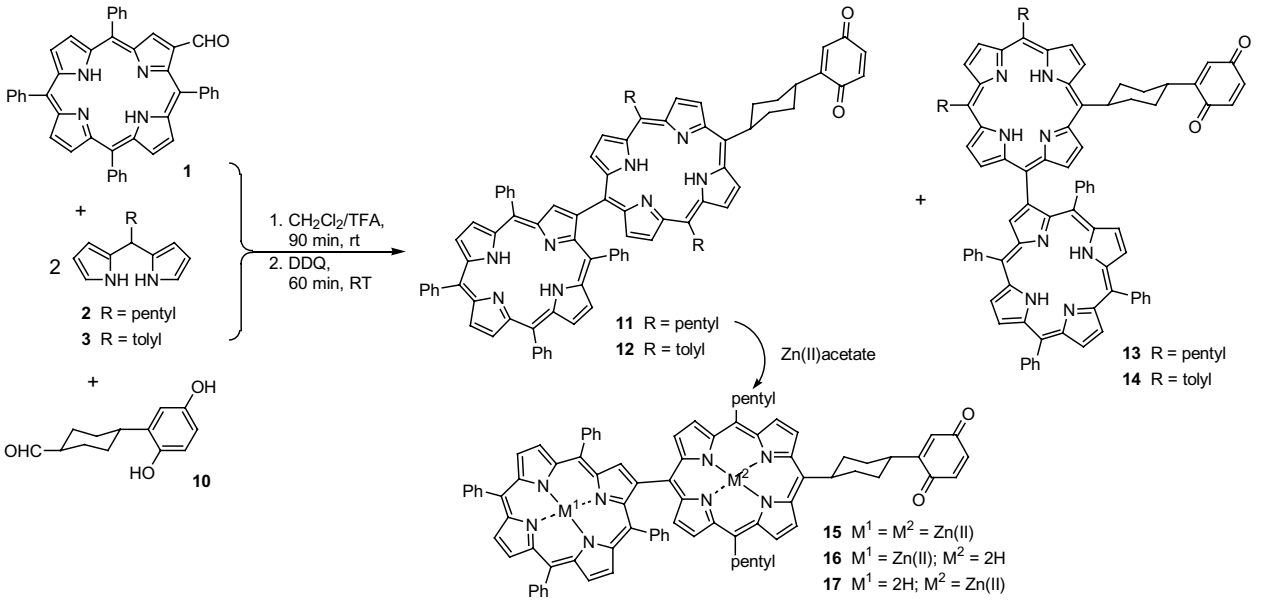


Figure 1. Molecular structure of **5** in the crystal. Hydrogen atoms have been omitted for clarity; thermal ellipsoids give 50% occupancy.

Secondly, the porphyrin tilt together with the known tilting of *meso*-aryl substituents gives rise to a unique structural feature that is not possible in *meso–meso*-linked dimers. Here the phenyl ring (at C20) in the TPP unit closest to the *meso*–β-linkage forms a π–π-stabilized complex with the tritolylporphyrin part. In general terms, the phenyl ring forms a π–π stack with a dipyrromethene part of the tritolylporphyrin. The phenyl *ipso*-carbon atom is separated from the respective *meso* carbon by only 3.004 Å. This structural feature also explains the stability and ease of separation of the two atropisomers found for the trimers (**6**,**7** and **8**,**9**). Evidence for a similar situation in solution comes from the selective shifts of the respective phenyl proton signals in ^{1}H NMR experiments[10,16] and from NOE experiments. Irradiation of the β-H in the DPnP part of **8** flanking the *meso*–β-linkage (β-2,8,12,18) gave a NOE with both the TPP-3-β-H and the 20-*o*-Ph-H, while irradiation of the *o*-Ph-H gave a NOE with the 20-*m*-Ph-H and the 2,8,12,18-β-H's.

In order to test whether the approach utilized above can be used for the construction of donor–acceptor compounds we again used **1** and dipyrromethanes as building blocks. Reaction of **1** and **2** in a 1:2:1 ratio with the aldehyde **10**[9b] gave two P–P–Q systems (Scheme 2).[15] One compound was identified as the expected P–P–Q **11** (8%), while the second component was identified as the scrambling product **13** (4%), with the 'middle' porphyrin carrying the P and Q substituents in 5,20-orientation. Likewise, reaction of **1** + **2** + **10** gave **12** and **14** in 9% and 6% yield, respectively.[16]

Amongst other indications, the ^{1}H signals for the β-pyrrole hydrogen atoms flanking the cyclohexane spacer are quite indicative for the different regioisomers. In **12** the DTP-3,7-β H signals appear as a broad singlet at 9.67 ppm at rt, indicating a cyclohexane-dependent dynamic process. At 323 K the broad signal is resolved into a doublet with $J \sim 5$ Hz. In **14** two broad singlets are observed at 9.65 and 9.40 ppm at 273 K. For the 2,8-β H



Scheme 2. Syntheses of P–P–Q triads.

atoms two doublets are found at 273 K at 8.71 and 8.94 ppm. In **12**, one doublet is found at 8.93 ppm for the respective H atoms. The UV–vis spectra for all dimers and P–P–Q's are characterized by a splitting of the Soret band into two bands at ~420 and ~440 nm and the long-wavelength Q-band at 655–665 nm. The *meso*–β–*meso* trimers have a split Soret band at 420, 455 nm and the long-wavelength Q-band at 672 nm. Corresponding results were observed upon metalation of **11** with zinc(II) acetate.[17]

Currently we are expanding the P–P–Q series to include systems with targeted variation of the frontier orbitals via substituent variation, optimize the reaction conditions to suppress scrambling, and will report on these compounds and their full spectroscopic investigation in due course.

Acknowledgements

This work was supported by a grant from the Deutsche Forschungsgemeinschaft (Se543/5-2).

References and notes

1. Gust, D.; Moore, T. A. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic: San Diego, 2000; Vol. 8, pp 153–190; Kurreck, H.; Huber, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 849–866; Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435–461.
2. Huber, M. *Eur. J. Org. Chem.* **2001**, 4379–4389.
3. Yang, S. I.; Seth, J.; Balasubramanian, T.; Kim, D.; Lindsey, J. S.; Holten, D.; Bocian, D. F. *J. Am. Chem. Soc.* **1999**, *121*, 4008–4018.
4. (a) Osuka, A.; Shimidzu, H. *Angew. Chem., Int. Ed.* **1997**, *36*, 135–137; Ogawa, T.; Nishimoto, Y.; Yoshida, N.; Ono, N.; Osuka, A. *Chem. Commun.* **1998**, 337–338; (b) Susumu, K.; Shimidzu, T.; Tanaka, K.; Segawa, H. *Tetrahedron Lett.* **1996**, *37*, 8399–8402; Khoury, R. G.; Jaquinod, K.; Smith, K. M. *Chem. Commun.* **1997**, 1057–1058; (c) Senge, M. O.; Feng, X. *Tetrahedron Lett.* **1999**, *40*, 4165–4168; *J. Chem. Soc., Perkin Trans. 1* **2000**, 3615–3621.
5. Ogawa, T.; Nishimoto, Y.; Yoshida, N.; Ono, N.; Osuka, A. *Angew. Chem., Int. Ed.* **1999**, *38*, 176–179.
6. Deng, Y.; Chang, C. K.; Nocera, D. G. *Angew. Chem., Int. Ed.* **2000**, *39*, 1066–1068.
7. (a) Wasielewski, M. R.; Johnson, D. G.; Niemczyk, M. P.; Gaines, G. L., III; O'Neil, M. P.; Svec, W. A. *J. Am. Chem. Soc.* **1990**, *112*, 6482–6488; Johnson, D. G.; Niemczyk, M. P.; Minsek, D. W.; Wiederrecht, G. P.; Svec, W. A.; Gaines, G. L., III; Wasielewski, M. R. *J. Am. Chem. Soc.* **1993**, *115*, 5692–5701; (b) Zheng, G.; Pandey, R. K.; Forsyth, T. P.; Kozyrev, A. N.; Dougherty, T. J.; Smith, K. M. *Tetrahedron Lett.* **1997**, *38*, 2409–2412; (c) Wiehe, A.; Senge, M. O.; Schäfer, A.; Speck, M.; Tannert, S.; Kurreck, H.; Röder, B. *Tetrahedron* **2001**, *57*, 10089–10110.
8. Molecular tapes with both *meso–meso* and β–β-linkages have also been prepared; they have extensive π-conjugation and are better suited for applications in photonics. Sugiura, K.-i.; Matsumoto, T.; Ohkouchi, S.; Naitoh, Y.; Kawai, T.; Takai, Y.; Ushiroda, K.; Sakata, Y. *Chem. Commun.* **1999**, 1957–1958; Tsuda, A.; Furuta, H.; Osuka, A. *J. Am. Chem. Soc.* **2001**, *123*, 10304–10321; Kamo, M.; Tsuda, A.; Nakamura, Y.; Aratani, N.; Furukawa, K.; Kato, T.; Osuka, A. *Org. Lett.* **2003**, *5*, 2079–2082; Tsuda, A.; Nakamura, Y.; Osuka, A. *Chem. Commun.* **2003**, 1096–1097.
9. (a) Lee, C.-.H.; Lindsey, J. S. *Tetrahedron* **1994**, *50*, 11427–11440; (b) von Gersdorff, J.; Kirste, B.; Kurreck, H. *Liebigs Ann. Chem.* **1993**, 897–903; This has proven to be an excellent acceptor component in PQ-systems: Elger, G.; Fuhs, M.; Müller, P.; von Gersdorff, J.; Wiehe, A.; Kurreck, H.; Möbius, K. *Mol. Phys.* **1998**, *95*, 1309–1323; Senge, M. O.; Speck, M.; Wiehe, A.; Dieks, H.;

Aguirre, S.; Kurreck, H. *Photochem. Photobiol.* **1999**, *70*, 206–216; (c) Andrioletti, B.; Rose, E. *J. Chem. Soc., Perkin Trans. 1* **2002**, 715–716.

10. Selected spectroscopic data: **4**: ^{1}H NMR (500 MHz, $CDCl_3$, TMS):[11] $\delta = -2.75$, -2.35 (each s, 2×2H, N*H*), 0.95 (t, 6H, 5,15-CH_2CH_3), 1.08 (t, 3H, 10-CH_2CH_3), 1.51 (sext., 4H, 5,15-CH_2CH_3), 1.65 (sext., 2H, 10-CH_2CH_3), 1.75 (quint., 4H, 5,15-$CH_2CH_2CH_3$), 1.92 (quint., 2H, 10-$CH_2CH_2CH_3$), 2.54 (sext., 4H, 5,15-$CH_2CH_2CH_2CH_3$), 2.66 (sext., 2H, 10-$CH_2CH_2CH_2CH_3$), 3.91 (t, 1H, 20-Ph_p), 4.6 (t, 2H, 10-$CH_2CH_2CH_2CH_2CH_3$), 4.91 (t, 4H, 5,15-$CH_2CH_2CH_2CH_2CH_3$), 5.04 (t, 2H, 20-Ph_m), 6.68 (d, 2H, 20-Ph_o), 7.63 (t, 1H, Ph_p), 7.72 (m, 5H, $Ph_{m,p}$), 7.82 (m, 3H, $Ph_{m,p}$), 8.17, 8.62 (each d, 2×1H, TPP-17,18-H_β), 8.20, 8.34, 8.6 (each d, 3×1H, Ph_o), 8.48, 9.13 (each d, 2×2H, TPnP-2,3,17,18-H_β), 8.89, 9.0 (dd, AB, 2×2H, TPP-7,8,12,13-H_β), 9.54 (dd, AB, TPnP-7,8,12,13-H_β), 9.65 (s, 1H, TPP 3-H_β); MS (EI, 80 eV, 350 °C); *m*/*z* (%): 1133 (10) [M^+], 1062 (3) [$M^+-C_5H_{11}$], 614 (5) [$M^+-C_{35}H_{43}N_4$=TPnP], 465 (10), 156 (100); UV–vis (CH_2Cl_2): λ_{max} (rel. ε)=420 (1.0), 440 (0.99), 521 (0.11), 563 (0.05), 594 (0.04), 654 (sh, 0.028), 665 nm (0.038). **6**: ^{1}H NMR (500 MHz, $CDCl_3$, TMS): $\delta = -2.65$ (s, 2H, DPnP-N*H*), -2.35 (br s, 4H, TPP-N*H*), 0.94 (t, 6H, CH_2CH_3), 1.53 (sext., 4H, CH_2CH_3), 1.70 (quint., 4H, $CH_2CH_2CH_3$), 2.52 (quint., 4H, $CH_2CH_2CH_2CH_3$), 4.80 (t, 2H, TPP-20-Ph_p), 4.88 (t, 4H, $CH_2CH_2CH_2CH_2CH_3$), 5.23 (t, 4H, TPP-20-Ph_m), 7.22 (d, 4H, TPP-20-Ph_o), 7.59 (t, 2H, TPP-5-Ph_p), 7.66 (t, 4H, $Ph_{m,p}$), 7.78 (m, 6H, $Ph_{m,p}$), 7.85 (m, 6H, $Ph_{m,p}$), 8.28 (dd, 4H, TPP-15-Ph_o), 8.36 (m, 4H, TPP-10-Ph_o), 8.39 (d, 2H, TPP-H-18$_\beta$), 8.45 (d, 4H, TPP-5-Ph_o), 8.63 (d, 4H, DPnP-3,7,13,17-H_β), 8.73 (d, 2H, TPP-17-H_β), 8.93 (AB system, 4H, TPP-12,13-H_β), 9.00 (AB system, 4H, TPP-7,8-H_β), 9.15 (d, 4H, DPnP-H-2,8,12,18-H_β), 9.57 (s, 2H, TPP-3-H_β); MS (EI, 80 eV, 380 °C); *m*/*z* (%): 1676 (15) [M^+], 838 (13) [M^{2+}], 614 (100) [M^+-1062=TPP]; UV–vis (CH_2Cl_2): λ_{max} (rel. ε)=420 (1.0), 455 (0.55), 520 (0.148), 592 (0.07), 669 nm (0.038). **8**: ^{1}H NMR (500 MHz, $CDCl_3$, TMS): $\delta = -2.79$ (s, 2H, DPnP-N*H*), -2.49 (br s, 4H, TPP-N*H*), 0.86 (t, 6H, CH_2CH_3), 1.45 (m, 4H, CH_2CH_3), 1.69 (m, 4H, $CH_2CH_2CH_3$), 2.51 (m, 4H, $CH_2CH_2CH_2CH_3$), 3.84 (t, 2H, TPP-20-Ph_p), 4.50 (t, 4H, TPP-20-Ph_m), 4.87 (m, 4H, $CH_2CH_2CH_2CH_2CH_3$), 6.74 (d, 4H, TPP-20-Ph_o), 7.70, (m, 6H, TPP-15-$Ph_{m,p}$), 7.76 (m, 6H, TPP-5-$Ph_{m,p}$), 7.81 (m, 6H, TPP-10-$Ph_{m,p}$), 8.15 (d, 2H, TPP-H-18$_\beta$), 8.18 (d, 4H, TPP-15-Ph_o), 8.32 (m, 4H, TPP-10-Ph_o), 8.53 (d, 4H, TPP-5-Ph_o), 8.59 (d, 2H, TPP-17-H_β), 8.66 (d, 4H, DPnP-3,7,13,17-H_β), 8.89 (AB system, 4H, TPP-12,13-H_β), 9.02 (AB system, 4H, TPP-7,8-H_β), 9.14 (d, 4H, DPnP-H-2,8,12,18-H_β), 9.82 (s, 2H, TPP-3-H_β); UV–vis (CH_2Cl_2): λ_{max} (rel. ε)=419 (1.0), 455 (0.77), 520 (0.17), 591 (0.08), 672 nm (0.057).
11. Abbreviations used in NMR assignments: DTP=ditolyporphyrin part; Q=quinone part, TPnP=tripentylporphyrin part; TPP=tetraphenylporphyrin part. Assignements are based on NOE and ^{1}H–^{1}H-COSY experiments.
12. Lecas-Nawrocka, A.; Boitrel, B.; Rose, E. *Tetrahedron Lett.* **1992**, *33*, 481–484; Littler, B. J.; Ciringh, Y.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 2864–2872.
13. Yoshia, N.; Ishizuka, T.; Osuka, A.; Jeong, D. H.; Cho, H. S.; Kim, D.; Matsuzaki, Y.; Nogami, A.; Tanaka, K. *Chem. Eur. J.* **2003**, *9*, 58–75.
14. Crystal data for **5**: $C_{85}H_{60}N_8{\cdot}3CH_2Cl_2$, $M = 1448.19$, triclinic, space group $P\bar{1}$, $a = 8.9128(19)$, $b = 10.369(2)$, $c = 19.784(5)$ Å, $\alpha = 84.25(2)$, $\beta = 87.57(2)$, $\gamma = 81.58(2)°$, $V = 1798.8(7)$ Å^3, $Z = 1$, $T = 130$ K, μ (Cu-K$_\alpha$)=2.601 cm^{-1}, 5064 unique reflections measured ($R_{int} = 0.0168$), 4687 reflections with $I > 2.0\sigma(I)$, refinement against $|F^2|$, $R1(I > 2.0\sigma(I)) = 0.0829$, *wR*2 (all data)=0.233, $S = 1.035$, $\rho_{max} = 0.839$, solvate molecules disordered. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-230767. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).
15. Typical procedure for P–P–Q's: Formyl porphyrin **1** (0.125 mmol, 80 mg), dipyrromethane **3** (59 mg, 0.125 mmol), and 0.125 mmol (28 mg) of aldehyde **10** were dissolved in 25 mL CH_2Cl_2. The solution was purged with Ar, treated with 96 μL TFA and stirred for 90 min. After addition of 114 mg (0.5 mmol) DDQ and stirring for 1 h the solution was neutralized with 0.17 mL triethylamine and washed with $NaHCO_3$ and water. The crude product was purified by filtration through silica eluting with CH_2Cl_2 followed by column chromatography on silica gel eluting with *n*-hexane/acetic acid ester (3.5:1, v/v). The main fraction was subjected to preparative HPLC (silica 5μ, diisopropyl ether/*n*-hexane=3:7) yielding **12** (15 mg, 9%) and **14** (10 mg, 6%). Although many other products can be formed under the reaction conditions, the target compounds are easily identified as they are red and nonfluorescent on TLC.
16. Selected spectroscopic data: **12**: ^{1}H NMR (500 MHz, $CDCl_3$, $SiMe_4$): $\delta = -2.89$, -2.40 (each br s, 2×1H, DTP: N*H*), -2.40 (s, 2H, TPP: N*H*), 2.02 (qd, 2H, DTP···CH_2CH-Q ax), 2.40 (br d, 2H, DTP···CH_2CH-Q eq), 2.67 (s, 6H, $C_6H_5CH_3$), 2.97 (m, 2H, DTP-$CHCH_2$···Q eq), 3.49 (tt, 1H, DTP···CH_2CH-Q ax), 4.06 (t, 1H, TPP-20-Ph_p), 4.43 (qd, 2H, DTP-$CHCH_2$···Q ax), 4.78 (t, 2H, TPP-20-Ph_m), 5.36 (tt, 1H, DTP-$CHCH_2$···Q ax), 6.86 (dd, 1H, Q: –C=CH–CO–C*H*=CH–CO–), 6.88 (m, 1H, Q: –C=C*H*–CO–CH=CH–CO–), 6.92 (m, 2H, TPP-20-Ph_o), 6.93 (d, 1H, Q: –C=CH–CO–CH=C*H*–CO–), 7.53 (m, 4H, $tolyl_m$), 7.76–7.60 (m, 6H, TPP-5,15-$Ph_{m,p}$), 7.82 (m, 3H, TPP-10-$Ph_{m,p}$), 8.03, 8.18 (each br d, 2×2H, $tolyl_o$), 8.20 (m, 2H, TPP-15-Ph_o), 8.28 (d, 1H, TPP-17-H_β), 8.30 (m, 2H, TPP-10-Ph_o), 8.44 (m, 2H, TPP-5-Ph_o), 8.55 (m, 4H, DTP-12,13,17,18-H_β), 8.63 (d, 1H, TPP-18-H_β), 8.88 (AB system, 2H, TPP-12,13-H_β), 8.93 (d, 2H, DTP-3,8-H_β), 8.98 (AB system, 2H, TPP-7,8-H_β), 9.63 (s, 1H, TPP-3-H_β), 9.67 (br s, 2H, DTP-2,7-H_β); MS (EI, 80 eV, 380 °C), *m*/*z* (%): 1293 (6) [M^++2H], 1103 (39), 1025 (41), 429 (22), 287 (30), 192 (100); UV–vis (CH_2Cl_2): λ_{max} (rel. ε)=253 (0.16), 423 (0.95), 438 (1.0), 521 (0.12), 560 (0.06), 597 (0.05), 658 nm (0.05). **14**: ^{1}H NMR (500 MHz, $CDCl_3$, $SiMe_4$): $\delta = -2.72$ (br s, 2H, DTP: N*H*), -2.36 (s, 2H, TPP: N*H*), 1.59 (m, 2H, DTP···CH_2CH-Q ax), 2.33 (m, 2H, DTP···CH_2CH-Q eq), 2.64, 2.76 (each s, 2×3H, $C_6H_5CH_3$), 2.93 (m, 2H, DTP-$CHCH_2$···Q eq), 3.37 (m, 3H, DTP···CH_2CH-Q ax, DTP-$CHCH_2$···Q ax), 3.94 (t, 1H, TPP-20-Ph_p), 4.64 (m, 2H, TPP-20-Ph_m), 5.27 (tt, 1H, DTP-$CHCH_2$···Q ax), 6.83 (m, 5H, TPP-20-Ph_o, Q: –C=C*H*–CO–C*H*=C*H*–CO–), 7.53 (m, 2H, $tolyl_m$), 7.58 (br d, 1H, TPP-5-Ph_m), 7.64 (m, 2H, TPP-5$Ph_{m,p}$), 7.72 (m, 5H, TPP-15-$Ph_{m,p}$, $tolyl_m$), 7.83 (m, 3H, TPP-10-$Ph_{m,p}$), 8.02 (m, 1H, $tolyl_o$), 8.06 (br d, 1H, TPP-5-Ph_o), 8.18 (m, 1H, $tolyl_o$), 8.20 (m, 3H, TPP-17-H_β, TPP-15-Ph_o), 8.26 (br d, 1H, TPP-5-Ph_o), 8.32 (m, 2H, TPP-10-Ph_o), 8.48 (m, 2H, $tolyl_o$), 8.58 (m, 2H, DTP-12,13-H_β), 8.63 (d, 1H, TPP-18-H_β), 8.71 (d, 1H, DTP-8-H_β), 8.82 (AB system, 2H, DTP-17,18-H_β), 8.89 (AB system, 2H, TPP-12,13-H_β), 8.94 (d, 1H, DTP-2-H_β), 9.00 (AB system, 2H, TPP-7,8-H_β), 9.40 (br s, 1H, DTP-7-H_β), 9.65 (br s, 1H, DTP-3-H_β), 9.68 (s, 1H, TPP-3-H_β); MS (EI, 80 eV, 380 °C), *m*/*z*

(%): 1293 (6) [M^++2H], 1103 (45), 1025 (57), 428 (5), 247 (30), 192 (100); UV–vis (CH_2Cl_2): λ_{max} (rel. ε)=252 (0.16), 421 (1.0), 443 (0.96), 522 (0.14), 559 (0.07), 597 (0.055), 658 nm (0.055).

17. UV–vis (CH_2Cl_2): λ_{max} (rel. ε)=**15**: 422 (1.0), 444 (0.95), 557 (0.12), 603 (0.036), ~635; **16**: 422 (0.98), 442 (1.0), 535 (sh), 552 (0.1), 610 (sh), 666 (0.028); **17**: 421 (1.0), 440 (0.91), 518 (0.11), 559 (0.09), 602 (0.06), 635 nm (0.015).