

## Synthesis and Diels–Alder reaction of a sapphyrin derivative

João P. C. Tomé,<sup>a,b</sup> Dong-Gyu Cho,<sup>a</sup> Jonathan L. Sessler,<sup>a,\*</sup> Maria G. P. M. S. Neves,<sup>b</sup>  
Augusto C. Tomé,<sup>b</sup> Artur M. S. Silva<sup>b</sup> and José A. S. Cavaleiro<sup>b,\*</sup>

<sup>a</sup>Department of Chemistry and Biochemistry, 1 University Station-A5300, The University of Texas at Austin,  
Austin, TX 78712-0165, USA

<sup>b</sup>Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

Received 29 December 2005; revised 14 February 2006; accepted 24 February 2006

Available online 15 March 2006

**Abstract**—Sapphyrins participate in Diels–Alder reactions with pentacene affording novel barrelene-fused sapphyrins. The new compounds were synthesized using traditional heating and microwave irradiation conditions. The experiments carried out under microwave irradiation proved cleaner, affording only the monoadduct and in higher yields.

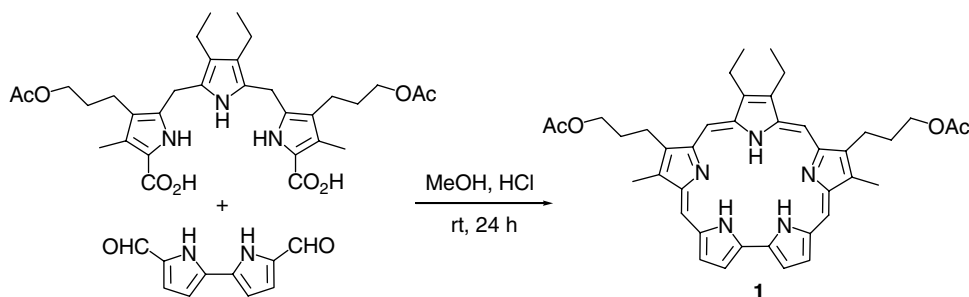
© 2006 Elsevier Ltd. All rights reserved.

Sapphyrins are among the best studied of all expanded porphyrins. They contain an aromatic 22  $\pi$ -electron aromatic periphery and possess a number of novel spectral and electronic features that have made them attractive for a range of applications, including those associated with anion recognition.<sup>1,2</sup> From a structural perspective, sapphyrins also bear analogy to the contracted porphyrin analogues, corroles, since both contain a bipyrrrolic subunit. Recently it was shown that corroles can participate in Diels–Alder and thermal [4+4] cycloadditions with pentacene.<sup>3</sup> It was thus anticipated that sapphyrins would also react with pentacene, giving rise to similar kinds of adducts. However, when the reaction between sapphyrin **1** and pentacene was carried out, important

differences were observed as compared to what is found in the case of corroles.

Sapphyrin **1**<sup>4</sup> was obtained in 18% yield from the reaction between an acetylated tripyrrromethane dicarboxylic acid<sup>5</sup> and 5,5'-diformyl-2,2'-bipyrrrole.<sup>6</sup> This chemistry, which is based on a known procedure, is summarized in [Scheme 1](#).<sup>7</sup>

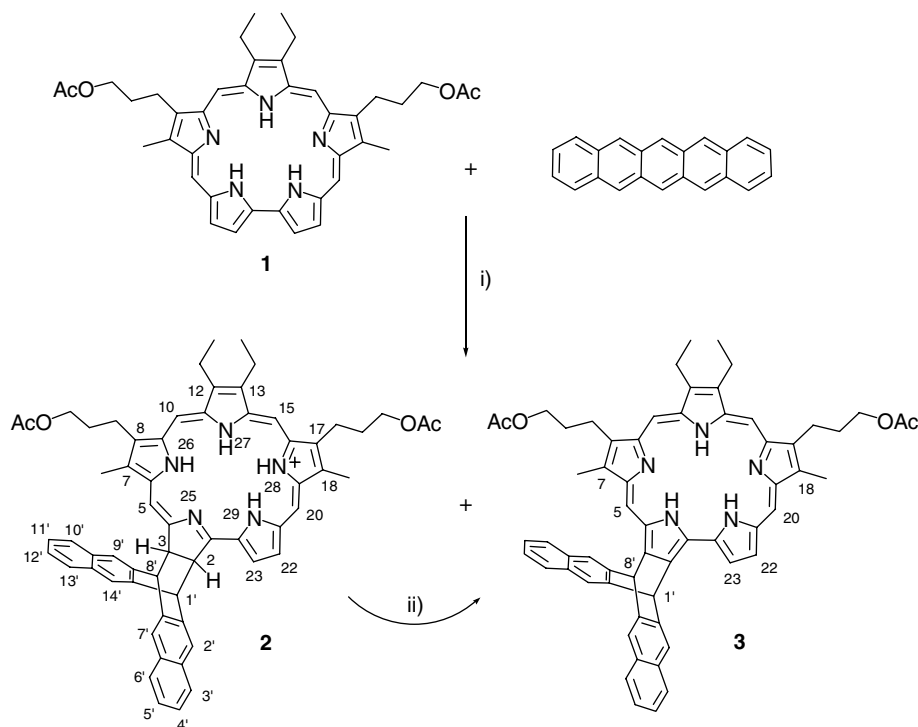
The Diels–Alder reaction between sapphyrin **1** and pentacene is shown in [Scheme 2](#). It was performed under thermal conditions by heating a 1,2,4-trichlorobenzene solution containing a 1:5 molar ratio of these two reactants at 200 °C for 5 h under a nitrogen atmosphere.<sup>8</sup>



**Scheme 1.**

**Keywords:** Sapphyrins; Diels–Alder reactions; Pentacene; Barrelene; Microwave irradiation.

\*Corresponding authors. Fax: +1 512 471 7550 (J.L.S.); +351 234 370 084 (J.A.S.C.); e-mail addresses: [sessler@mail.utexas.edu](mailto:sessler@mail.utexas.edu); [jcavaleiro@dq.ua.pt](mailto:jcavaleiro@dq.ua.pt)



**Scheme 2.** Reagents and conditions: (i) 1,2,4-trichlorobenzene, 200 °C, 5 h, N<sub>2</sub> or 1,2,4-trichlorobenzene, MW irradiation, 200 °C, 1 h, N<sub>2</sub>, (ii) DDQ, dry toluene, rt, 2 h, N<sub>2</sub>.

The reaction mixture was purified by first column chromatography and then preparative TLC. The compound with the higher *R<sub>f</sub>* value on silica gel TLC plates was obtained in only a trace quantity. Its mass spectrum (FAB<sup>+</sup>, *m/z* = 1217) led to its assignment as a bis-adduct.<sup>9</sup> The main product was identified as the mono-adduct **2** (21% yield), while the compound with lower *R<sub>f</sub>* value was shown to be **3** (5% yield).<sup>10,11</sup> Compound **3**, which presumably resulted from the dehydrogenation of monoadduct **2**, was also obtained from the oxidation of **2** with DDQ in dry toluene at room temperature.<sup>12</sup>

The advantages of microwave irradiation over conventional heating in terms of engendering certain organic transformations are becoming increasingly well appreciated.<sup>13</sup> For instance, it was shown quite recently that the use of this technique results in an impressive improvement in the yield of the Diels–Alder reactions between *meso*-tetrakis(pentafluorophenyl)porphyrin and pentacene or naphthacene.<sup>14</sup> Recognizing this and being aware of the fact that the sapphyrin cycloadducts are obtained in low yields under the experimental conditions described above, we decided to use microwave irradiation in the hope of improving the outcome of the reaction. In fact, when a solution of sapphyrin **1** and pentacene (1.4 equiv) was irradiated at ca. 200 °C for 1 h, compound **2** was obtained in 51% yield; compound **3** and the bisadduct were not formed.<sup>15</sup> Thus, in this case the use of a microwave irradiation-based procedure allows for a shorter reaction time and obviates the need to use a large excess of pentacene. As importantly, a cleaner reaction mixture is obtained; this facilitates purification and allows the product to be obtained in pure form after passage through a small silica gel column.

The structures of compounds **2** and **3** were deduced from their 1D and 2D NMR spectra (COSY, NOESY, HSQC and HMBC). The <sup>1</sup>H NMR spectrum of compound **2** displays signals corresponding to the 34 aliphatic protons of the alkyl groups on the periphery of the sapphyrin. However, an analysis of the HSQC spectrum indicates the existence of four other aliphatic protons ( $\delta$  6.03, 6.35–6.39 and 6.85 ppm), which correlate with carbon resonances at  $\delta$  51.6, 51.7, 55.5 and 56.7 ppm. These findings are consistent with the notion that cycloadduct **2** is a reduced sapphyrin. The <sup>1</sup>H NMR spectrum of compound **2** also contains four singlets at lower frequency values ( $\delta$  –1.71, –2.89, –3.16 and –3.98 ppm) corresponding to the NH resonances. The COSY spectrum shows a cross peak between the singlet at  $\delta$  –2.89 ppm and those at  $\delta$  9.84 and 10.34 ppm; these signals were thus attributed to the resonances of protons H-22 and H-23. The later resonance presents NOE cross peaks with those of H-2 ( $\delta$  6.85 ppm) and H-1' ( $\delta$  6.35–6.39 ppm), supporting its assignment to H-23. From the NOESY spectrum it was also possible to confirm the close proximity between H-5 ( $\delta$  10.09 ppm), H-3 ( $\delta$  6.35–6.39 ppm) and CH<sub>3</sub>-7 ( $\delta$  3.99 ppm), and also between H-20 ( $\delta$  10.51 ppm) and CH<sub>3</sub>-18 ( $\delta$  3.88 ppm). The other two downfield singlets at 10.43 and 11.06 ppm showed NOE cross peaks with those of the CH<sub>2</sub> groups of the ethyl and acetyloxypropyl substituents, and were assigned to the H-10 and H-15 proton resonances. The HSQC and HMBC spectra of compound **2** allowed the assignment of almost all the carbon resonances.

In the case of compound **3**, the <sup>1</sup>H and COSY NMR spectra allowed the assignment of the resonances of the aliphatic protons. However, an unequivocal assignment

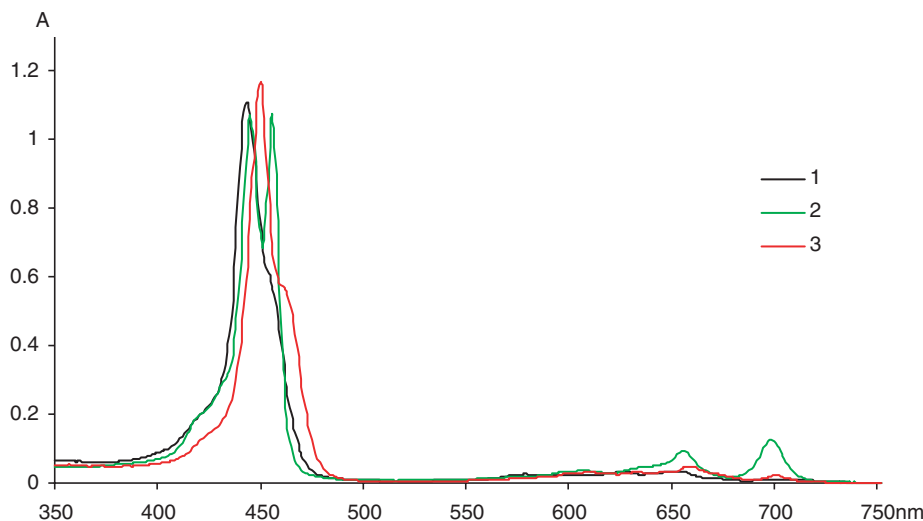


Figure 1. UV-vis spectra of sapphyrin **1**, adduct **2** and compound **3** in  $\text{CH}_2\text{Cl}_2$  at  $3.5 \mu\text{M}$ .

of the main features of this  $^1\text{H}$  NMR spectrum was based on the NOESY spectrum. In the  $^1\text{H}$  NMR spectrum of compound **3** one can observe the proton resonances of H-22 and H-23 (two doublets with a small coupling constant,  $J = 3.3$  Hz), as well as those of H-1' and H-8' (two singlets). In the NOESY spectrum it was possible to observe NOE cross peaks between the doublet at  $\delta$  11.40 ppm and the singlet at  $\delta$  12.07 ppm, thus allowing assignment of these resonances to H-23 and H-1', respectively. This same spectrum allows the close proximity between H-22 (d,  $\delta$  10.80 ppm) and H-20 (s,  $\delta$  12.07 ppm) to be inferred, along with interactions between this latter proton and  $\text{CH}_3$ -18 (s,  $\delta$  4.35 ppm) and also between H-5 (s,  $\delta$  12.25 ppm) and  $\text{CH}_3$ -7 (s,  $\delta$  4.52 ppm).

Comparing the  $^1\text{H}$  NMR spectra of compounds **2** and **3** it was possible to observe the disappearance of H-2 and H-3 proton resonances and a shift to higher frequency values for the NH,  $\beta$ - and *meso*-proton resonances of compound **3** relative to those of **2**. Most likely, this is due to the increase in the ring magnetic anisotropy (increasing electron ring current and planarity). A detailed analysis of the  $^1\text{H}$ ,  $^{13}\text{C}$  and 2D NMR spectra of **3** allowed the assignment of the other proton and carbon resonances.

Figure 1 shows the UV-vis spectra of sapphyrin **1**, adduct **2** and the dehydrogenated adduct **3** at the same concentration ( $3.5 \mu\text{M}$ ). The most notable features are observed for adduct **2**: it shows strong Q bands at 656 and 699 nm and its Soret band is split (445 and 456 nm), with a bathochromic shift relative to the Soret band of sapphyrin **1** (443 nm) being observed. The splitting of the Soret band is ascribed to the strong asymmetry of the molecule structure, a conclusion that is consistent with the observed NMR spectral features. The very small red shift is rationalized in terms of reduced intramolecular electronic coupling between the sapphyrin and pentacene subunits.

In conclusion, in spite of the apparent structural analogies between corroles and sapphyrins, the two macro-

cyclic systems behave differently in their reaction with pentacene. While corroles give rise to dehydrogenated compounds derived from [4+2] mono- and bisadducts, as well as [4+4] cycloadducts, sapphyrins give mainly [4+2] monoadducts and do not yield detectable quantities of the corresponding [4+4] cycloadducts.

#### Acknowledgements

Thanks are due to the Texas Advanced Technology Program, the National Science Foundation (grant no. CHE-0515670 to J.L.S.), the University of Aveiro, Fundação para a Ciência e a Tecnologia and POCI 2010 (FEDER) (Project POCI/QUI/57589/2004 and the Organic Chemistry Research Unit). We also thank Dr. Diana C. G. A. Pinto for her assistance in the microwave experiments. J.P.C.T. thanks FCT for a post-doctoral grant (SFRH/BPD/5630/2001).

#### Supplementary data

Supplementary data (1D and 2D NMR spectra for compounds **1–3**) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.02.144.

#### References and notes

- Sessler, J. L.; Seidel, D. *Angew. Chem., Int. Ed.* **2003**, *42*, 5134–5175.
- Sessler, J. L.; Gebauer, A.; Weghorn, J. S. In *The Porphyrin Handbook—Heteroporphyrins, Expanded Porphyrins and Related Macrocycles*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: New York, 2000; Vol. 2.
- Barata, J. F. B.; Silva, A. M. G.; Faustino, M. A. F.; Neves, M. G. P. M. S.; Tomé, A. C.; Silva, A. M. S.; Cavaleiro, J. A. S. *Synlett* **2004**, 1291–1293.
- Synthesis of sapphyrin **1**: Conc. HCl (0.53 mL) was added dropwise to a stirred solution of the tripyrromethane dicarboxylic acid (1.71 g, 2.86 mmol) and 5,5'-diformyl-

- 2,2'-bipyrrole (540 mg, 2.87 mmol) in MeOH (2.9 L) at room temperature. The reaction was monitored by TLC and deemed complete after 24 h. The solution was neutralized with triethylamine and concentrated to a few milliliters under reduced pressure. The crude mixture was purified by passing through a plug of silica gel using CH<sub>2</sub>Cl<sub>2</sub>/MeOH (95:5) as eluent. Sapphyrin **1** was then purified by column chromatography (neutral alumina) using THF/petroleum ether (1:1) as eluent. Sapphyrin **1** was crystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane, yielding green crystals (680 mg, 18% yield). Mp = 138–140 °C, *R*<sub>f</sub> (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/MeOH (93:7)) = 0.17, <sup>1</sup>H NMR (500.13 MHz, CDCl<sub>3</sub>) δ: −5.22 (s, 3H, NH), 2.20 (t, *J* = 7.7 Hz, 6H, CH<sub>2</sub>CH<sub>3</sub>), 2.32 (s, 6H, OCOCH<sub>3</sub>), 2.88 (qui, *J* = 7.0 Hz, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAc), 4.02 (s, 6H, CH<sub>3</sub>-7,18), 4.61–4.66 (m, 12H, CH<sub>2</sub>CH<sub>3</sub> and CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAc), 9.83 and 10.18 (2d, *J* = 3.7 Hz, 4H, pyrrole-β-H), 10.69 and 10.78 (2s, 4H, meso-H); <sup>13</sup>C NMR (125.77 MHz, CDCl<sub>3</sub>) δ: 12.4 (CH<sub>3</sub>-7,18), 18.5 (CH<sub>2</sub>CH<sub>3</sub>), 21.0 and 24.2 (CH<sub>2</sub>CH<sub>3</sub> and CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAc), 21.2 (OCOCH<sub>3</sub>), 32.3 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAc), 64.6 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAc), 89.2, 100.9, 123.4, 129.4, 133.3, 135.2, 135.7, 136.1, 136.6, 137.5, 138.3, 140.7, 171.4 (OCOCH<sub>3</sub>); UV-vis (CH<sub>2</sub>Cl<sub>2</sub>), λ<sub>max</sub> (log ε): 443 (5.54), 578 (4.05), 625 (4.08), 649 (4.00), 715 (3.53) nm; HRMS (FAB<sup>+</sup>) *m/z*: calcd for C<sub>40</sub>H<sub>46</sub>N<sub>5</sub>O<sub>4</sub> (M+H)<sup>+</sup> = 660.3550, found 660.3581.
- Sessler, J. L.; Mody, T.; Hemmi, G. W.; Lynch, V. *Inorg. Chem.* **1993**, *32*, 3175–3187.
  - Bauer, V. J.; Clive, D. L. J.; Dolphin, D.; Paine, J. B., III; Harris, F. L.; King, M. M.; Loder, J.; Wang, S.-W. C.; Woodward, R. B. *J. Am. Chem. Soc.* **1983**, *105*, 6429–6436.
  - Sessler, J. L.; Cyr, M. J.; Lynch, V.; McGhee, E.; Ibers, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 2810–2813.
  - A solution of sapphyrin **1** (20.0 mg, 30.3 μmol) and pentacene (42.0 mg, 151 μmol, 5 equiv) in 1,2,4-trichlorobenzene (2 mL) was stirred for 5 h at 200 °C under a nitrogen atmosphere. The reaction mixture was directly purified by column chromatography over silica gel. The 1,2,4-trichlorobenzene was eluted off with hexane and the products were then eluted off using a gradient of THF in hexane. The unreacted sapphyrin **1** (6.6 mg, 33%) was recovered using CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>3</sub>N (2%) as the eluent. Adduct **2** was further purified by preparative TLC using THF/hexane (1:1) as the eluent, followed by crystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane (5.97 mg, 21% yield).
  - Due to the small amount of the bisadduct available, its structure could not be deduced. However, in analogy to the bisadduct formed upon reaction of pentacene with tris(pentafluorophenyl)corrole (Ref. 3), we propose that in this bisadduct the two pentacene units are located on the two pyrroles of the bipyrrole subunit.
  - Adduct **2**: mp > 250 °C, *R*<sub>f</sub> (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/MeOH (93:7)) = 0.50, <sup>1</sup>H NMR (500.13 MHz, CDCl<sub>3</sub>) δ: −3.98, −3.16, −1.71 (3s, 3H, NH-26,27,28), −2.89 (s, 1H, NH-29), 1.94 and 1.98 (2t, *J* = 7.6 Hz, 6H, CH<sub>2</sub>CH<sub>3</sub>), 2.26 and 2.27 (2s, 6H, OCOCH<sub>3</sub>), 2.73–2.77 and 2.83–2.88 (2m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAc), 3.88 (s, 3H, CH<sub>3</sub>-18), 3.99 (s, 3H, CH<sub>3</sub>-7), 4.29–4.42 and 4.51–4.63 (2m, 12H, CH<sub>2</sub>CH<sub>3</sub> and CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAc), 6.03 (d, *J* = 3.4 Hz, 1H, H-8'), 6.26 (t, *J* = 7.4 Hz, 1H, Ar-H), 6.35–6.39 (m, 4H, H-3, H-1' and 2 Ar-H), 6.70, 7.17, 8.36 and 8.39 (4s, 4H, H-2',14' and H-7',9'), 6.76 (d, *J* = 8.3 Hz, 1H, Ar-H), 6.85 (dd, *J* = 3.3 and 8.7 Hz, 1H, H-2), 7.60–7.62 (m, 2H, Ar-H), 8.05–8.09 (m, 2H, Ar-H), 9.84 (d, *J* = 3.4 Hz, 1H, H-22), 10.09 (s, 1H, H-5), 10.34 (d, *J* = 3.4 Hz, 1H, H-23), 10.43 and 11.06 (2s, 2H, H-10,15), 10.51 (s, 1H, H-20). <sup>13</sup>C NMR (125.77 MHz, CDCl<sub>3</sub>) δ: 12.4 (CH<sub>3</sub>-7,18), 18.1 and 18.5 (CH<sub>2</sub>CH<sub>3</sub>), 20.3, 20.6, 23.6 and 24.4 (CH<sub>2</sub>CH<sub>3</sub> and CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAc), 21.19 and 21.21 (OCOCH<sub>3</sub>), 31.5 and 32.3 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAc), 51.6 (C-8'), 51.7 (C-1'), 55.5 (C-2), 56.7 (C-3), 64.2 and 64.5 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAc), 87.5 and 92.6 (C-10,15), 96.3 and 96.4 (C-5,20), 121.5 (C-23), 122.2, 122.8 and 123.0 (C-2',14' and C-7',9'), 123.9 and 124.0 (Ar-CH), 124.7 (C-22), 126.0, 126.4, 126.6 and 127.89 (Ar-CH), 127.89, 127.93, 128.4, 130.9, 131.1, 131.2, 132.9, 133.0, 133.1, 134.5, 134.7, 135.7, 135.9, 136.5, 136.9, 137.2, 137.6, 138.2, 139.7, 141.6, 141.8, 141.9, 158.9, 161.8, 171.4 and 171.5 (OCOCH<sub>3</sub>). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>), λ<sub>max</sub> (log ε): 445 (5.49), 456 (5.49), 609 (4.00), 656 (4.43), 699 (4.56) nm; HRMS (FAB<sup>+</sup>) *m/z*: calcd for C<sub>62</sub>H<sub>60</sub>N<sub>5</sub>O<sub>4</sub> (M+H)<sup>+</sup> = 938.4645, found 938.4634.
  - Compound **3**: mp > 250 °C, *R*<sub>f</sub> (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/MeOH (93:7)) = 0.21, <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>/TFA) δ: −6.58 and −5.70 (2 br s, 3H and 2H, NH), 2.27 (t, *J* = 7.4 Hz, 6H, CH<sub>2</sub>CH<sub>3</sub>), 2.34 and 2.35 (2s, 6H, OCOCH<sub>3</sub>), 2.92–3.06 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAc), 4.35 (s, 3H, CH<sub>3</sub>-18), 4.52 (s, 3H, CH<sub>3</sub>-7), 4.67–4.73 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAc), 4.81–4.87 (m, 4H, CH<sub>2</sub>CH<sub>3</sub>), 4.90–4.94 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAc), 7.41–7.44 and 7.85–7.87 (2 m, 8H, H-3', 13', 4', 12', 5', 11' and 6', 10'), 8.01 (s, 1H, H-8'), 8.27 (s, 1H, H-1'), 8.57 and 8.58 (2s, 4H, H-2',14' and 7',9'), 10.80 (d, *J* = 3.3 Hz, 1H, H-22), 11.40 (d, *J* = 3.3 Hz, 1H, H-23), 11.91 (br s, 2H, H-10,15), 12.07 (s, 1H, H-20), 12.25 (s, 1H, H-5). <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>/TFA) δ: 12.9 and 13.2 (CH<sub>3</sub>-7,18), 18.3 (CH<sub>2</sub>CH<sub>3</sub>), 21.0 and 21.1 (CH<sub>2</sub>CH<sub>3</sub> and OCOCH<sub>3</sub>), 24.1 and 24.2 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAc), 31.70 and 31.76 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAc), 49.8 (C-8'), 51.1 (C-1'), 65.3 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAc), 92.3 (C-10,15), 98.5 (C-5), 101.6 (C-20), 122.3, 122.6 (C-23), 123.6 (C-2',14' and C-7',9'), 124.8, 125.1, 126.6, 127.69 and 127.74 (C-3',13', 4',12', 5',11' and 6',10'), 128.8, 129.0, 130.8 (C-22), 131.3, 131.9, 132.0, 133.3, 133.5, 135.5, 135.6, 135.8, 135.9, 136.0, 139.4, 139.7, 139.9, 141.7, 141.8, 144.4, 144.6, 151.7, 174.3 (OCOCH<sub>3</sub>). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>), λ<sub>max</sub> (log ε): 450 (5.50), 610 (3.94), 634 (3.96), 647 (3.97), 659 (4.13), 701(3.85) nm. HRMS (FAB<sup>+</sup>) *m/z*: calcd for C<sub>62</sub>H<sub>58</sub>N<sub>5</sub>O<sub>4</sub> (M+H)<sup>+</sup> = 936.4489, found 936.4533.
  - A solution of **2** (8.4 mg, 8.9 μmol) in dry toluene (2 mL) was stirred with DDQ (20 mg, 88 μmol, 9.9 equiv) for 2 h at room temperature under a nitrogen atmosphere. The reaction mixture was directly passed through a short alumina column to remove the DDQ. The products were separated by column chromatography (silica gel) using first hexane and then a gradient of hexane/THF as the eluents. Compound **3** was further purified by preparative TLC using hexane/THF (1:1) as the eluent, followed by crystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane (7.1 mg, 85% yield).
  - Review: Kappe, C. O. *Angew. Chem., Int. Ed.* **2004**, *43*, 5260–5285.
  - Silva, A. M. G.; Tomé, A. C.; Neves, M. G. P. M. S.; Cavaleiro, J. A. S.; Kappe, C. O. *Tetrahedron Lett.* **2005**, *46*, 4723–4726.
  - A solution of sapphyrin **1** (20.0 mg, 30.3 μmol) and pentacene (11.5 mg, 41.4 μmol, 1.4 equiv) in trichlorobenzene (2 mL), stirred with a teflon-coated magnetic stirrer bar, was irradiated for 1 h at ca. 200 °C (850 W) under a nitrogen atmosphere, at normal pressure, in a MicroSynth apparatus. The adduct **2** was purified by column chromatography (silica gel) using hexane/THF (1:1) as the eluent. It was then crystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane (14.5 mg, 51% yield). Unreacted sapphyrin **1** (7.3 mg, 37%) was recovered using CH<sub>2</sub>Cl<sub>2</sub>/NET<sub>3</sub> (2%) as the eluent.