Supporting Information

Synthesis and Luminescence Properties of U-Shaped Polycyclic Molecules Containing Syn-Facial Functionalized Quinoxaline Rings

Teh-Chang Chou,* Kung-Ching Liao, and Jin-Ju Lin

*Department of Chemistry and Biochemistry, National Chung Cheng University,
Minsyong, Chiayi, 621, Taiwan*

Instrumentation and General Information

^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded using a Bruker DPX-400 (400 MHz) at ambient temperature. Chemical shift (δ) and coupling constant (J) were expressed in unit of ppm and Hz, respectively. The chemical shift of CHCl_3 was calibrated at δ 7.26 ppm in ^1H NMR spectra and δ 77.0 ppm in ^{13}C NMR spectra. Multiplicities of splitting pattern in ^1H NMR spectra were abbreviated: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). The ^1H NMR spectra data were expressed in the following manner: chemical shift (multiplicity, coupling constant, number of hydrogen). All ^{13}C NMR spectra were recorded with the protons completely decoupled. The number of attached hydrogen on the carbon atom was determined by the Distortionless Enhancement by Polarization Transfer (DEPT) analysis.

Melting points were determined in capillaries on a Thomas-Hoover apparatus and Büchi Melting Point B-450 apparatus, the temperature are uncorrected.

Infrared spectroscopy (IR) were obtained using a JASCO 400-plus spectrometer, and configured with JASCO Spectra Manager software. Samples were suspended in a KBr disk or dissolved in CHCl_3 solution. The spectral data were recorded in unit of wavenumber (cm^{-1}).

Mass spectroscopy (MS) were measured with a Finnigan/Thermo Quest MAT 95XL spectrometer. Electron-Impact (EI) mass spectra were obtained at an electron beam energy of 70 eV, unless otherwise specified. MS spectral data were reported at m/z , and the relative intensities (%) were expressed in parenthesis, where the base peak was calibrated to be 100. High resolution mass spectra (HRMS) were obtained using same spectrometer. Fast atom bombardment (FAB) mass spectroscopy were collected on a Finnigan/Thermo Quest MAT 95XL double focusing mass spectrometer with a resolution of 8000 and 3000 for HR and LR FAB-mass spectra, respectively. The source accelerating voltage was operated at 10 kV with Xe gun for FAB-mass spectra, using 3-nitrobenzyl alcohol as matrix.

Elemental analysis was analyzed using a Heraeus CHN-O-S-Rapid and Heraeus elemental vario EL III elemental analyzers.

Ultraviolet/visible (UV/vis) absorption spectra were measured with HP 8453 UV-Visible Photodiode Array. Spectrometric grade solvent and quartz cell ($1 \times 1 \text{ cm}^2$) were used. The extinctions coefficient (ϵ) was obtained from: $\epsilon = A / bc$, where A is the absorbance, b is the path of quartz cell (1 cm), c is the molar concentration of sample solution. The UV/vis spectral data were expressed in the following manner: absorption λ_{max} (extinction coefficient). The molar concentration of the sample solution was about $1.5 \times 10^{-5} \text{ M}$, unless otherwise specified. Fluorescence emission spectra were obtained using a Varian Cary-Eclipse fluorescence spectrometer. Spectrometric grade solvents and quartz cell ($1 \times 1 \text{ cm}^2$) were used. The fluorescence spectra data were expressed in the following manner: emission λ_{max} .

The X-ray crystallographic data were recorded with a Bruker AXS SMART APEX CCD X-ray diffractometer. Graphite monochromatized Mo K α radiation [λ = 0.71073 Å] and temperature of 298 (2) K were used. The CCD data were processed with SAINT and the structures were solved by direct method (SHELXS-97) and refined on F^2 by full-matrix least-squares techniques (SHELXL-97).

Thin-layer chromatography (TLC) was performed on E. Merck silica gel 60 F₂₅₄ plate (0.20 mm). The developed TLC sheets were examined under UV light. Unless otherwise stated, all reagents were purchased from Sigma-Aldrich, E. Merck, Acros, Fluka, or TCI and used without further purification; solvents were used without further distillation. All reactions were stirred with a magnetic stir bar under nitrogen atmosphere, unless otherwise specified.

Experimental Section

General procedure for the preparation of bis- α -ketones B :

A suspension of NaIO₄ (2.50 mmol) and RuCl₃·3H₂O (0.11 mmol) in water (3.4 mL) was added in portions to an ice-cooled suspension of syn-bis-DA-adduct **A** (1.0 mmol) in CHCl₃ (10 mL) and CH₃CN (10 mL) over a period of hours, monitored by TLC and ¹H NMR. The mixture was added water (50 mL) and extracted with CHCl₃ (2 x 15 mL). The combined organic phase was washed with water (2 x 20 mL), dried over MgSO₄, and evaporated. Purification by recrystallization with chloroform afforded yellow platelets.

(1 β ,2 β ,5 β ,6 α ,9 α ,10 β ,13 β ,14 α)-1,6,9,14-tetrachloro-17,17,18,18-tetramethoxy-hexacyclo[6.6.1.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}]heptadecane-4,5,11,12-tetraone. Reaction time 48 hours, yield 80 %. M.p. 282-284 °C (decomp); IR (KBr): 2998 (m), 2852 (m), 1797 (s), 1769 (s), 1221 (s), 1192 (s), 903 (s); ¹H NMR (400 MHz, CDCl₃): δ 3.72 (s, 6H), 3.51 (s,

6H), 2.73 (brs, 4H), 2.60 (brs, 2H), 0.86 (brs, 2H); MS (70 eV, EI): 546 (11) [M+6]⁺, 544 (46) [M+4]⁺, 542 (100) [M+2]⁺, 540 (69) [M]⁺; Anal. Calcd for C₂₁H₂₀Cl₄O₈ (542.19): C, 46.52; H, 3.72; O, 23.61; found: C, 46.13; H, 3.72; O, 23.28.

(1 β ,2 β ,3 α ,6 α ,7 β ,8 β ,9 β ,10 α ,13 α ,14 β)-3,6,10,13-tetrachloro-16,16,17,17-tetramethoxy-pentacyclo[12.2.1.1^{6,9}.0^{2,13}.0^{5,10}]octadecane-7,8,15,16-tetraone. Reaction time 24 hours, yield 91 %. M.p. 294-296 °C (decomp); IR (KBr): 2953 (m), 1797 (s), 1771 (s), 1224 (s), 1197

(s), 903 (s); ¹H NMR (400 MHz, CDCl₃): δ 3.79 (s, 6H), 3.56 (s, 6H), 2.96 (d, J = 8.4 Hz, 4H), 1.92 (d, J = 9.6 Hz, 4H), 1.23 (dd, J = 8.4, 7.3 Hz, 4H); ¹³C NMR (100

MHz, CDCl₃): δ 187.6 (s), 101.7 (s), 80.1 (s), 52.9 (q), 52.3 (q), 42.7 (d), 20.3 (t); MS (70 eV, EI): 560 (3) [M+4]⁺, 558 (6) [M+2]⁺, 556 (5) [M]⁺, 59 (100); Anal. Calcd for C₂₂H₂₄Cl₄O₈ (558.23): C, 47.33; H, 4.33; O, 22.93; found: C, 47.17; H, 4.32; O, 22.91.

(1 α ,2 β ,5 α ,6 β ,9 β ,10 α ,13 β ,14 α)-1,6,9,14-tetrachoro-17,17,18,18-tetramethoxypentacyclo[12.2.1.1^{6,9}.0^{2,13}.0^{5,10}]octadecane-7,8,15,

16-tetraone. Reaction time 72 hours, yield 84 %. M.p. 294-296 °C (decomp); IR (KBr): 2991 (m), 2951 (m), 2905 (m), 2847 (m), 1794 (s), 1766 (s), 1468 (s), 1287 (s); ¹H NMR (400 MHz, CDCl₃): δ 3.69 (s, 6H), 3.52 (s, 6H), 2.82 (d, *J* = 10.2 Hz, 4H), 2.08 (d, *J* = 11.6 Hz, 4H), 0.76 (m, 4H); MS (FAB): 564 (3) [M+8]⁺, 556 (7) [M]⁺; 154 (100); Anal. Calcd for C₂₂H₂₄Cl₄O₈ (558.23): C, 47.33; H, 4.33; O, 22.93; found: C, 47.23; H, 4.66; O, 22.53.

General procedure for the preparation of syn-bis-quinoxalines C and 42:

Into a solution of bis- α -diketone **B** (0.50 mmol) in chlorobenzene (12.5 mL) containing a catalytic amount of zinc acetate was added *o*-phenylenediamine (1.10 mmol) under reflux for hours, monitored by TLC and ¹H NMR. The reaction mixture was filtered to remove salt and the filtrate was concentrated. The residue was purified *via* recrystallization from EtOH/CHCl₃ (3/2 by vol.) to afford pure adduct.

(1 α ,2 β ,4 β ,5 α ,16 α ,17 β ,19 β ,20 α)-7,14,22,29-tetraaza-1,5,16,20-tetrachloro-31,31,32,32-tetramethoxy-nonacyclo[18.10.1.1^{5,16}.0^{2,19}.0^{4,1}.7.0^{6,15}.0^{8,13}.0^{21,30}.0^{23,28}]dotriacontane-6(15),7,9,11,13,21(30),22,

24,26,28-decaene. Reaction time 15 hours, yield 92 %. M.p. 310-313 °C (decomp); IR (KBr): 2915 (m), 1196 (m), 753 (m); ¹H NMR (400 MHz, CDCl₃): δ 7.71 (dd, *J* = 6.4, 3.5 Hz, 4H), 7.44 (dd, *J* = 6.4, 3.5 Hz, 4H), 3.74 (s, 6H), 3.34 (s, 6H), 2.88 (dd, *J* = 7.2, 4.6 Hz, 4H), 1.98 (d, *J* = 13.6 Hz, 2H), -1.12 (d, *J* = 13.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 151.8 (s), 141.2 (s), 129.6 (d), 128.6 (d), 111.3 (s), 74.8 (s), 52.3 (q), 51.9 (q), 43.3 (d), 19.5 (t); UV/Vis (CHCl₃): λ_{abs} (ϵ mol⁻¹dm³cm⁻¹) 242 (47000), 317 nm (14000); Emission (CHCl₃): λ_{em} 395 nm; MS (70 eV, EI): 676 (7) [M+4]⁺, 674 (21) [M+2]⁺, 672 (12) [M]⁺, 44 (100); Anal. Calcd for C₃₂H₂₈Cl₄N₄O₄ (674.40): C, 56.99; H, 4.18; N, 8.31; O, 9.49; found: C, 56.65; H, 4.32; N, 8.09; O, 9.36.

(1 α ,2 β ,5 β ,6 α ,17 α ,18 β ,21 β ,22 α)-8,15,24,31-tetraaza-1,6,17,22-tetrachloro-33,33,34,34-tetramethoxynonacyclo[20.10.1.1^{6,17}.0^{2,21}.0^{5,18}.0^{7,10}.0^{9,14}.0^{23,32}.0^{25,30}]tetratriacontane-

7(10),8,10,12,14, 23(32),24,26,28,30-decaene. Reaction time 12 hours, yield 92 %. M.p. 318-321

$^{\circ}\text{C}$ (decomp); IR (KBr): 2949 (m), 1197 (s), 768 (m); ^1H NMR (400 MHz, CDCl_3): δ 8.11 (dd, $J = 6.4, 3.5$ Hz, 4H), 7.69 (dd, $J = 6.4, 3.5$ Hz, 4H), 3.88 (s, 6H), 3.44 (s, 6H), 3.26 (d, $J = 8.4$ Hz, 4H), 1.93 (d, $J = 9.6$ Hz, 4H), 0.44 (dd, $J = 8.4, 7.3$ Hz, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ 152.5 (s), 142.2 (s), 129.8 (d), 129.2 (d), 110.6 (s), 76.1 (s), 52.4 (q), 52.3 (q), 44.6 (d), 20.5 (t); UV/Vis (CHCl_3): λ_{abs} (ϵ $\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$) 243 (64000), 317 (18000); Emission (CHCl_3): λ_{em} 390 nm; MS (70 eV, EI) 702 (w) $[\text{M}+2]^+$, 700 (w) $[\text{M}]^+$, 74 (100); Anal. Calcd for $\text{C}_{34}\text{H}_{32}\text{Cl}_4\text{N}_4\text{O}_4$ (702.45): C, 8.13; H, 4.59; N, 7.98; O, 9.11; found: C, 58.37; H, 4.58; N, 7.95; O, 9.46.

(1 α ,2 β ,4 β ,5 α ,16 α ,17 β ,19 β ,20 α)-7,14,22,29-tetraaza-1,5,16,20-tetrachloro-31,31,32,32-tetramethoxy-10,11,25,26-tetramethyl-nonacyclo[18.10.1.1^{5,16}.0^{2,19}.0^{4,17}.0^{6,15}.0^{8,13}.0^{21,30}.0^{23,28}]dotriacontane-6(15),7,9,11,13,21(30),22,24,26,28-decaene. Reaction time 44 hours, yield 88 %. M.p. $>300^{\circ}\text{C}$; IR (KBr): 2982 (w), 2949 (s), 2839 (m), 1499 (s), 1194 (s); ^1H NMR (400 MHz, CDCl_3): δ 7.52 (s, 4H), 3.72 (s, 6H), 3.32 (s, 6H), 2.86 (dd, $J = 7.2, 4.6$ Hz, 4H), 2.39 (s, 12H), 1.95 (ddd, $J = 13.6, 4.4, 4.0$ Hz, 2H), -1.06 (d, $J = 13.6$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 150.7 (s), 140.0 (s), 139.0 (s), 127.9 (d), 111.2 (s), 74.8 (s), 52.1 (q), 51.8 (q), 43.3 (d), 20.0 (q), 19.3 (t); UV/Vis (CHCl_3): λ_{abs} (ϵ $\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$) 246 (71000), 327 (21000); Emission (CHCl_3): λ_{em} 387 nm; MS (FAB): 736 (5) $[\text{M}+8]^+$, 734 (13) $[\text{M}+6]^+$, 732 (29) $[\text{M}+4]^+$, 730 (23) $[\text{M}+2]^+$, 728 (8) $[\text{M}]^+$, 289 (100); HRMS (FAB) Calcd for $\text{C}_{36}\text{H}_{37}\text{Cl}_4\text{N}_4\text{O}_4$ $[\text{M}+\text{H}]^+$: 729.1569; found: 729.1577; Anal. Calcd for $\text{C}_{36}\text{H}_{36}\text{Cl}_4\text{N}_4\text{O}_4$ (730.51): C, 59.19; H, 4.97; N, 7.67; O, 8.76; found: C, 59.39; H, 5.18; N, 7.86; O, 8.59.

(1 α ,2 β ,5 β ,6 α ,17 α ,18 β ,21 β ,22 α)-8,15,24,31-tetraaza-1,6,17,22-tetrachloro-33,33,34,34-tetramethoxy-11,12,27,28-tetramethyl-nonacyclo[20.10.1.1^{6,17}.0^{2,21}.0^{5,18}.0^{7,10}.0^{9,14}.0^{23,32}.0^{25,30}]tetraatriacontane-7(10),8,10,12,14,23(32),24,26,28,30-decaene. Reaction time 18 hours, yield 88 %. M.p. $>300^{\circ}\text{C}$; IR (KBr): 2982 (w), 2945 (s), 2839 (m), 1499 (s), 1194 (s); ^1H NMR (400 MHz, CDCl_3): δ 7.87 (s, 4H), 3.86 (s, 6H), 3.43 (s, 6H), 3.22 (d, $J = 8.4$ Hz, 4H), 2.42 (s, 12H), 1.90 (d, $J = 9.6$ Hz, 4H), 0.39 (dd, $J = 8.4, 7.3$ Hz, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ 151.5 (s), 141.0 (s), 140.1 (s), 128.5 (d), 110.7 (s), 76.2 (s), 52.4 (q), 52.2 (q), 44.7 (d), 20.5 (t), 20.1 (q); UV/Vis (CHCl_3): λ_{abs} (ϵ $\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$) 250 (58000), 328 (17000); Emission (CHCl_3): λ_{em} 380 nm; MS (FAB): 764 (12) $[\text{M}+8]^+$, 762 (46) $[\text{M}+6]^+$, 760 (84) $[\text{M}+4]^+$, 758 (63) $[\text{M}+2]^+$, 757 (4)

$[M+1]^+$, 75 (100).

(1 α ,2 β ,4 β ,5 α ,16 α ,17 β ,19 β ,20 α)-7,14,22,29-tetraaza-1,5,16,20-tetrachloro-10,11,25,26,31,31,32,32-octamethoxynonacyclo[18.10.1.1⁵,16.0^{2,19}.0^{4,17}.0^{6,15}.0^{8,13}.0^{21,30}.0^{23,28}]dotriacontane-6(15),7,9,11,13,21(30),

22,24,26,28-decaene. Reaction time 48 hours, yield 86 %. M.p. 322-325 °C (decomp); IR (KBr): 2950 (m), 1514 (m), 1251 (m), 1193 (s), 1007 (s); ¹H NMR (400 MHz, CDCl₃): δ 7.08 (s, 4H), 3.95 (s, 12H), 3.72 (s, 6H), 3.34 (s, 6H), 2.85 (dd, J = 7.2, 4.6 Hz, 4H), 1.92 (d, J = 13.6 Hz, 2H), -1.14 (d, J = 13.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 152.0 (s), 149.3 (s), 138.4 (s), 111.7 (s), 106.8 (d), 74.9 (s), 56.2 (q), 52.3 (q), 51.8 (q), 43.6 (d), 19.5 (t); UV/Vis (CHCl₃): λ_{abs} (ϵ mol⁻¹dm³cm⁻¹) 248 (26000), 346 (24000) nm; Emission (CHCl₃): λ_{em} 390 nm; MS (FAB): 795 (23) $[M+H+2]^+$, 793 (18) $[M+H]^+$, 307 (100); Anal. Calcd for C₃₆H₃₆Cl₄N₄O₈ (794.51): C, 54.42; H, 4.57; N, 7.05; O, 16.11, found: C, 54.60; H, 4.88; N, 7.25; O, 16.37.

21

(1 α ,2 β ,5 β ,6 α ,17 α ,18 β ,21 β ,22 α)-8,15,24,31-tetraaza-1,6,17,22-tetrachloro-11,12,27,28,33,33,34,34-octamethoxynonacyclo[20.10.1.1^{6,17}.0^{2,21}.0^{5,18}.0^{7,10}.0^{9,14}.0^{23,32}.0^{25,30}]tetratriacontane-7(10),8,10,1

2,14,23(32),24,26,28,30-decaene. Reaction time 24 hours, yield 88 %. M.p. 364-368 °C (decomp); IR (KBr): 2949 (m), 1506 (s), 1240 (s), 1193 (m), 1003 (m); ¹H NMR (400 MHz, CDCl₃): δ 7.44 (s, 4H), 3.97 (s, 12H), 3.86 (s, 6H), 3.44 (s, 6H), 3.23 (d, J = 8.4 Hz, 4H), 1.91 (d, J = 9.6 Hz, 4H), 0.42 (dd, J = 8.4, 7.3 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 152.3 (s), 150.0 (s), 139.1 (s), 111.1 (s), 107.4 (d), 76.3 (s), 56.4 (q), 52.4 (q), 52.2 (q), 44.9 (d), 20.6 (t); UV/Vis (CHCl₃): λ_{abs} (ϵ mol⁻¹dm³cm⁻¹) 244 (36000), 357 (33000)nm; Emission (CHCl₃): λ_{em} 381 nm; MS (FAB): 823 (9) $[M+3]^+$, 821 (5) $[M+1]^+$, 154 (100); Anal. Calcd for C₃₈H₄₀Cl₄N₄O₈ (822.56): C, 55.49; H, 4.90; N, 6.81; O, 15.56; found: C, 55.36; H, 4.99; N, 6.40; O, 15.36.

22

(1 α ,2 β ,4 β ,5 α ,16 α ,17 β ,19 β ,20 α)-7,14,22,29-tetraaza-1,5,10,11,16,20,25,26-octachloro-31,31,32,32-tetramethoxynonacyclo[18.10.1.1^{5,16}.0^{2,19}.0^{4,17}.0^{6,15}.0^{8,13}.0^{21,30}.0^{23,28}]dotriacontane-6(15),7,9,11,13,21(30),22,24,26,28-decaene. Reaction time 30 hours, yield 90 %. M.p. >300 °C; IR (KBr): 3083 (w), 2982 (m), 2950 (s), 2922 (m), 2884 (m), 1474 (s), 1194 (s); ¹H NMR (400 MHz, CDCl₃): δ 7.94 (s, 4H), 3.72 (s, 6H), 3.33 (s, 6H), 2.89 (dd, J = 7.2, 4.6 Hz, 4H), 1.97 (d, J = 13.6 Hz, 2H), -1.19 (d, J = 13.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 153.2 (s), 139.8 (s), 134.8 (s),

23

129.1 (d), 111.1 (s), 74.6 (s), 52.4 (q), 52.0 (q), 42.9 (d), 19.6 (t); UV/Vis (CHCl₃): λ_{abs} (ϵ mol⁻¹dm³cm⁻¹) 247 (53000), 330 (21000) nm; Emission (CHCl₃): λ_{em} 397 nm; MS (FAB): 816 (1) [M+8]⁺, 814 (2) [M+6]⁺, 812 (1) [M+4]⁺, 149 (100); Anal. Calcd for C₃₂H₂₄Cl₈N₄O₄ (812.18): C, 47.32; H, 2.98; N, 6.90; O, 7.88; found: C, 47.30; H, 3.19; N, 6.62; O, 8.05.

(1 α ,2 β ,5 β ,6 α ,17 α ,18 β ,21 β ,22 α)-8,15,24,31-tetraaza-1,6,11,12,17,22,27,28-octachloro-33,33,34,34-tetramethoxy-nonacyclo[20.10.1.1^{6,17}.0^{2,21}.0^{5,18}.0^{7,10}.0^{9,14}.0^{23,32}.0^{25,30}]tetratria-contane-7(10),8,10,12,

24

14,23(32),24,26,28,30-decaene. Reaction time 24 hours, yield 92 %.

M.p. >300 °C; IR (KBr): 3083 (w), 2981 (m), 2950 (s), 2845 (m), 1474 (s), 1194 (s); ¹H NMR (400 MHz, CDCl₃): δ 8.23 (s, 4H), 3.87 (s, 6H), 3.42 (s, 6H), 3.23 (d, J = 8.4 Hz, 4H), 1.90 (d, J = 9.6 Hz, 4H), 0.40 (dd, J = 8.4, 7.3 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 153.7 (s), 140.8 (s), 134.4 (s), 130.0 (d), 110.4 (s), 75.9 (s), 52.4 (q), 52.3 (q), 44.4 (d), 20.4 (t); UV/Vis (CHCl₃): λ_{abs} (ϵ mol⁻¹dm³cm⁻¹) 249 (59000), 329 (17000) nm; Emission (CHCl₃): λ_{em} 391 nm; MS (FAB): 837 (4) [M+2]⁺, 307 (100); HRMS (FAB) Calcd for C₃₄H₂₉Cl₈N₄O₈ [M+H]⁺: 836.9697; found: 836.9706; Anal. Calcd for C₃₄H₂₈Cl₈N₄O₈ (840.23): C, 48.60; H, 3.36; N, 6.67; O, 7.62; found: C, 48.87; H, 3.66; N, 7.08; O, 7.69.

(1 α ,2 β ,4 β ,5 α ,16 α ,17 β ,19 β ,20 α)-7,14,22,29-tetraaza-1,5,16,20-tetachloro-31,31,32,32-tetramethoxy-10,11,25,26-tetranitrononacyclo[18.10.1.1^{5,16}.0^{2,19}.0^{4,17}.0^{6,15}.0^{8,13}.0^{21,30}.0^{23,28}]dotriacontane-

25

6(15),7,9,11,13,21(30),22,24,26,28-decaene. Reaction time 96 hours,

yield 85 %. M.p. >300 °C; IR (KBr): 3080 (m), 2998 (m), 2954 (m), 2895 (w), 2846 (m), 1541 (s), 1353 (s), 1197 (s); ¹H NMR (400 MHz, CDCl₃): δ 8.43 (s, 4H), 3.76 (s, 6H), 3.34 (s, 6H), 3.01 (dd, J = 7.2, 4.6 Hz, 4H), 2.07 (d, J = 13.6 Hz, 2H), -1.22 (d, J = 13.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 157.4 (s), 141.9 (s), 141.7 (s), 126.2 (d), 111.5 (s), 74.5 (s), 52.6 (q), 52.3 (q), 42.8 (d), 19.8 (t); UV/Vis (CHCl₃): λ_{abs} (ϵ mol⁻¹dm³cm⁻¹) 255 nm (48000); MS (FAB): 856 (2) [M+4]⁺, 854 (2) [M+2]⁺, 154 (100); HRMS (FAB) Calcd for C₃₂H₂₅Cl₄N₈O₁₂ [M+H]⁺: 853.0346; found: 853.0333; Anal. Calcd for C₃₂H₂₄Cl₄N₈O₁₂ (854.39): C, 44.98; H, 2.83; N, 13.12; O, 22.47; found: C, 44.95; H, 3.12; N, 13.07; O, 22.57.

(1 α ,2 β ,5 β ,6 α ,17 α ,18 β ,21 β ,22 α)-8,15,24,31-tetraaza-1,6,17,22-tetrachloro-33,33,34,34-tetramethoxy-11,12,27,28-tetranitro- nonacyclo[20.10.1.1^{6,17}.0^{2,21}.0^{5,18}.0^{7,10}.0^{9,14}.0^{23,32}.0^{25,30}]tetratria-contane-7(10),8,10,12,14,23(32),24,26,28,30-decaene. Reaction time 34 hours, yield

84 %. M.p. >300 °C; IR (KBr): 3080 (m), 2999 (m), 2954 (m), 2898 (w), 2846 (m), 1541 (s), 1352 (s), 1197 (s); ¹H NMR (400 MHz, CDCl₃): δ 8.68 (s, 4H), 3.90 (s, 6H), 3.43 (s, 6H), 3.30 (d, *J* = 8.4 Hz, 4H), 1.96 (d, *J* = 9.6 Hz, 4H), 0.40 (dd, *J* = 8.4, 7.3 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 157.8 (s), 142.8 (s), 142.4 (s), 127.0 (d), 110.7 (s), 75.9 (s), 52.7 (q), 52.6 (q), 44.4 (d), 20.5 (t); UV/Vis (CHCl₃): λ_{abs} (ε mol⁻¹dm³cm⁻¹) 261 nm (42000); MS (FAB): 886 (2) [M+6]⁺, 884 (5) [M+4]⁺, 882 (3) [M+2]⁺, 138 (100); HRMS (FAB) Calcd for C₃₄H₂₈Cl₄N₈O₁₂ [M+H]⁺: 881.0659; found: 881.0664; Anal. Calcd for C₃₄H₂₈Cl₄N₈O₁₂ (882.44): C, 46.28; H, 3.35; N, 12.70; O, 21.76; found: C, 46.60; H, 3.73; N, 12.69; O, 21.72.

26

(1α,2β,4β,5α,20α,21β,23β,24α)-7,18,26,37-tetraaza-1,5,20,24-tetrachloro-39,39,40,40-tetramethoxyundecacyclo[22.14.1.1^{5,20}.0^{2,23}.0^{4,21}.0^{6,19}.0^{8,17}.0^{10,15}.0^{25,38}.0^{27,36}.0^{29,34}]tetracontane-6(19),7,9,11,13,15,17,25(38),26,28,

30,32,34,36-tetradecaene. Reaction time 18 hours, yield 89 %. M.p. >300 °C; IR (KBr): 3056 (w), 2981 (m), 2948 (m), 2843 (m), 1551 (m), 1456 (m), 1189 (s); ¹H NMR (400 MHz, CDCl₃): δ 8.08 (s, 4H), 7.52 (dd, *J* = 6.4, 3.5 Hz, 4H), 7.25 (dd, *J* = 6.4, 3.5 Hz, 4H), 3.75 (s, 6H), 3.34 (s, 6H), 2.93 (dd, *J* = 7.2, 4.6 Hz, 4H), 2.07 (d, *J* = 13.6 Hz, 2H), -0.75 (d, *J* = 13.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 152.4 (s), 137.3 (s), 132.7 (s), 127.7 (d), 126.8 (d), 110.3 (s), 74.9 (s), 52.3 (q), 52.0 (q), 43.2 (d), 19.6 (t); UV/Vis (CHCl₃): λ_{abs} (ε mol⁻¹dm³cm⁻¹) 270 (108000), 360 (9000)nm; Emission (CHCl₃): λ_{em} 514 nm; MS (FAB): 778 (4) [M+6]⁺, 776 (8) [M+4]⁺, 774 (8) [M+2]⁺, 772 (3) [M+6]⁺, 136 (100); HMRS (FAB) Calcd for C₄₀H₃₃Cl₄N₄O₄ [M+H]⁺: 773.1256, found: 773.1253; Anal. Calcd for C₄₀H₃₂Cl₄N₄O₄ (774.52): C, 62.03; H, 4.16; N, 7.23; O, 8.26; found: C, 61.84; H, 4.18; N, 6.91; O, 8.54.

27

(1α,2β,5β,6α,21α,22β,25β,26α)-8,19,28,38-tetraaza-1,6,21,26-tetrachloro-41,41,42,42-tetramethoxyundecacyclo[24.14.1.1^{6,21}.0^{2,25}.0^{5,22}.0^{7,20}.0^{9,18}.0^{11,16}.0^{27,40}.0^{29,38}.0^{31,36}]dotetracontane-7(20),8,10,12,14,

16,18,27(40),28,30,32,34,36-tetradecaene. Reaction time 24 hours, yield 87 %. M.p. >300 °C; IR (KBr): 3056 (w), 2981 (m), 2947 (m), 2843 (m), 1551 (m), 1456 (m), 1189 (s); ¹H NMR (400 MHz, CDCl₃): δ 8.66 (s, 4H), 8.02 (dd, *J* = 6.4, 3.5 Hz, 4H), 7.54 (dd, *J* = 6.4, 3.5 Hz, 4H), 3.91 (s, 6H), 3.47 (s, 6H), 3.39 (d, *J* = 8.4 Hz, 4H), 1.98 (d, *J* = 9.6 Hz, 4H), 0.59 (dd, *J* = 8.4, 7.3 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 153.3 (s), 138.6 (s), 133.4 (s), 128.4 (d), 127.8

28

(d), 127.0 (d), 109.7 (s), 76.2 (s), 52.5 (q), 52.3 (q), 44.5 (d), 20.5 (t); UV/Vis (CHCl₃): λ_{abs} (ϵ mol⁻¹dm³cm⁻¹) 274 (136000), 367 (14000)nm; Emission (CHCl₃): λ_{em} 479 nm; MS (FAB) ---; HMRS (FAB) Calcd for C₄₂H₃₇Cl₄N₄O₄ [M+H]⁺: 801.1569; found: 801.1565; Anal. Calcd for C₄₂H₃₆Cl₄N₄O₄ (802.57): C, 62.85; H, 4.52; N, 6.98; O, 7.97; found: C, 62.51; H, 4.73; N, 6.79; O, 8.11.

(1 α ,2 β ,5 α ,6 β ,21 β ,22 α ,25 β ,26 α)-8,19,28,38-tetraaza-1,6,21,26-tetrachloro-41,41,42,42-tetramethoxyundecacyclo[24.14.1.1^{6,21}.0^{2,25}.0^{5,22}.

0^{7,20}.0^{9,18}.0^{11,16}.0^{27,40}.0^{29,38}.0^{31,36}]dotetra-contane-7(20),8,10,12,14,

16,18,27(40),28,30,32,34,36-tetra-decaene. Reaction time 10 hours,

yield 90 %. M.p. >300 °C; IR (KBr): 3056 (w), 2981 (m), 2947 (m),

2843 (m), 1551 (m), 1456 (m), 1189 (s); ¹H NMR (400 MHz, CDCl₃):

δ 8.79 (s, 4H), 8.14 (dd, J = 6.4, 3.5 Hz, 4H), 7.64 (dd, J = 6.4, 3.5 Hz,

4H), 3.61 (s, 6H), 3.37 (s, 6H), 2.72 (d, J = 10.2 Hz, 4H), 2.15 (d, J =

11.6 Hz, 4H), 0.19 (dd, J = 10.2, 9.6 Hz, 4H); ¹³C NMR (100 MHz,

CDCl₃): δ 153.3 (s), 138.7 (s), 133.4 (s), 128.3 (d), 127.8 (d), 127.0 (d),

109.2 (s), 75.8 (s), 52.2 (q), 51.8 (q), 49.3 (d), 22.1 (t); UV/Vis

(CHCl₃): λ_{abs} (ϵ mol⁻¹dm³cm⁻¹) 279 (152000), 367 (14000)nm;

Emission (CHCl₃): λ_{em} 479 nm; MS (FAB): 807 (3) [M+H+6]⁺, 805 (8) [M+H+4]⁺, 803 (7)

[M+H+2]⁺, 154 (100); Anal. Calcd for C₄₂H₃₆Cl₄N₄O₄ (802.57): C, 62.85; H, 4.52; N, 6.98; O,

7.97; found: C, 62.81; H, 4.72; N, 7.14; O, 7.81.

General procedure for the preparation of the quinoxaline-attached α -diketones D:

Into a solution of bis- α -diketone **B** (0.50 mmol) in chlorobenzene (12.5 mL) containing a catalytic amount of zinc acetate was added *o*-phenylenediamine (0.55 mmol) under reflux for hours, monitored by TLC and ¹H NMR. The reaction mixture was filtered to remove salt and the filtrate was concentrated. The residue was purified *via* recrystallization from EtOH/CHCl₃ (3/1 by vol.) to afford pure adduct.

(1 α ,2 β ,4 β ,5 α ,8 α ,9 β ,11 β ,12 α)-14,21-diaza-1,5,8,12-tetrachloro-23,23,24,24-tetramethoxy-heptacyclo[10.10.1.1^{5,8}.0^{2,11}.0^{4,9}.0^{13,22}.0^{15,20}]tetracosane-13(22),14,16,18,20

-pentaene-6,7-dione. Reaction time 6 hours, yield 98 %; M.p. 224-226

°C (decomp); IR (KBr): 2950 (m), 1795 (m), 1769 (m), 1198 (s), 757

(m); ¹H NMR (400 MHz, CDCl₃): δ 8.19 (dd, J = 6.4, 3.5 Hz, 2H), 7.81

(dd, J = 6.4, 3.5 Hz, 2H), 3.80 (s, 3H), 3.78(s, 3H), 3.46 (s, 3H), 3.40 (s,

3H), 2.96 (dd, J = 7.2, 4.4 Hz, 2H), 2.77 (dd, J = 7.2, 4.8 Hz, 2H), 1.99

(d, $J = 13.6$ Hz, 2H), -0.35 (d, $J = 13.6$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 187.1 (s), 151.6 (s), 142.2 (s), 130.4 (d), 129.4 (d), 111.7 (s), 102.4 (s), 79.1 (s), 74.8 (s), 52.7 (q), 52.4 (q), 52.1 (q), 43.8 (d), 41.8 (d), 19.0 (t); UV/Vis (CHCl_3): λ_{abs} ($\epsilon \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$) 244 (30000), 319 (8100)nm; Emission (CHCl_3): 393, 476 nm; MS (70 eV, EI): λ_{em} 606 (11) $[\text{M}+6]^+$, 604 (47) $[\text{M}+4]^+$, 602 (100) $[\text{M}+2]^+$, 600 (65) $[\text{M}]^+$; Anal. Calcd for $\text{C}_{26}\text{H}_{24}\text{Cl}_4\text{N}_2\text{O}_6$ (602.29): C, 51.85; H, 4.02; N, 4.65; O, 15.94; found: C, 51.79; H, 3.71; N, 4.70; O, 15.92.

(1 α ,2 β ,4 β ,5 α ,8 α ,9 β ,11 β ,12 α)-14,21-diaza-1,5,8,12-tetrachloro-23,23,24,24-tetramethoxy-17,18-dimethylheptacyclo[10.10.1.1^{5,8}.0^{2,11}.0^{4,9}.0^{13,22}.0^{15,20}]tetracosane-13(22),14,16,18,20-pentaene-6,7-dione.

Reaction time 10 hours, yield 91 %. M.p. 227-229 °C (decomp); IR (KBr): 2950 (m), 2846 (w), 1798 (s), 1771 (s), 1496 (m), 1458 (m), 1195 (s); ^1H NMR (400 MHz, CDCl_3): δ 7.92 (s, 2H), 3.75 (s, 3H), 3.67 (s, 3H), 3.45 (s, 3H), 3.37 (s, 3H), 2.92 (dd, $J = 7.2, 4.4$ Hz, 2H), 2.75 (dd, $J = 7.2, 4.8$ Hz, 2H), 2.45 (s, 6H), 1.96 (ddd, $J = 13.6, 4.4, 4.0$ Hz, 2H), -0.37 (d, $J = 13.6$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 187.2 (s), 150.5 (s), 141.0 (s), 140.9 (s), 128.6 (d), 111.8 (s), 102.4 (s), 79.2 (s), 74.8 (s), 52.6 (q), 52.4 (q), 52.0 (q), 52.0 (q), 46.9 (d), 41.8 (d), 20.3 (q), 18.9 (t); UV/Vis (CHCl_3): λ_{abs} ($\epsilon \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$) 253 (37000), 344 (12000)nm; Emission (CHCl_3): λ_{em} 373, 467 nm; MS (FAB): 636 (5) $[\text{M}+8]^+$, 634 (14) $[\text{M}+6]^+$, 632 (28) $[\text{M}+4]^+$, 630 (28) $[\text{M}+2]^+$, 628 (12) $[\text{M}]^+$, 77 (100); HRMS (FAB) Calcd for $\text{C}_{28}\text{H}_{29}\text{Cl}_4\text{N}_2\text{O}_6$ $[\text{M}+\text{H}]^+$: 629.0780; found: 629.0789; Anal. Calcd for $\text{C}_{28}\text{H}_{28}\text{Cl}_4\text{N}_2\text{O}_6$ (630.34): C, 53.35; H, 4.48; N, 4.44; O, 15.23; found: C, 53.20; H, 4.37; N, 4.44; O, 15.25.

(1 α ,2 β ,4 β ,5 α ,8 α ,9 β ,11 β ,12 α)-14,21-diaza-1,5,8,12-tetrachloro-17,18,23,23,24,24-hexamethoxyheptacyclo[10.10.1.1^{5,8}.0^{2,11}.0^{4,9}.0^{13,22}.0^{15,20}]tetracosane-13(22),14,16,18,20-pentaene-6,7-dione.

Reaction time 16 hours, yield 92 %. M.p. 224-225 °C (decomp.); IR (KBr): 2952 (m), 1800 (m), 1772 (s), 1505 (s); ^1H NMR (400 MHz, CDCl_3): δ 7.49 (s, 2H), 4.06 (s, 6H), 3.76 (s, 3H), 3.69 (s, 3H), 3.46 (s, 3H), 3.40 (s, 3H), 2.92 (dd, $J = 7.2, 4.4$ Hz, 2H), 2.77 (dd, $J = 7.2, 4.8$ Hz, 2H), 1.98 (d, $J = 13.6$ Hz, 2H), -0.36 (d, $J = 13.6$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 187.2 (s), 152.8 (s), 148.9 (s), 139.3 (s), 112.2 (s), 107.5 (d), 102.4 (s), 79.2 (s), 74.8 (s), 56.4 (q), 52.7 (q), 52.4 (q), 52.1 (q), 52.0 (q), 44.1 (d), 41.8 (d), 19.0 (t); UV/Vis (CHCl_3): λ_{abs} ($\epsilon \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$) 251 (21000), 361 (21000)nm; Emission (CHCl_3): λ_{em} 390, 475 nm; MS (FAB): 663 (100) $[\text{M}+2]^+$; Anal. Calcd for $\text{C}_{28}\text{H}_{28}\text{Cl}_4\text{N}_2\text{O}_8$ (662.34): C, 50.77; H, 4.26; N, 4.23; O, 19.32; found: C, 50.62; H, 4.28; N, 4.37;

O, 19.18.

(1 α ,2 β ,4 β ,5 α ,8 α ,9 β ,11 β ,12 α)-14,21-diaza-1,5,8,12,17,18-hexachloro-23,23,24,24-tetra
methoxyheptacyclo[10.10.1.1^{5,8}.0^{2,11}.0^{4,9}.0^{13,22}.0^{15,20}]tetracosane-

13(22),14,16,18,20-pentaene-6,7-dione. Reaction time 12 hours, yield 96 %. M.p. 218-220 °C (decomp.); IR (KBr): 2952 (s), 1801 (m), 1769 (s), 1470 (s); ¹H NMR (400 MHz, CDCl₃): δ 8.30 (s, 2H), 3.76 (s, 3H), 3.69 (s, 3H), 3.47 (s, 3H), 3.39 (s, 3H), 2.96 (dd, J = 7.2, 4.4 Hz, 2H), 2.77 (dd, J = 7.2, 4.8 Hz, 2H), 1.98 (d, J = 13.6 Hz, 2H), -0.38 (d, J = 13.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 187.2 (s), 153.0 (s), 140.8 (s), 135.2 (s), 130.1 (d), 111.7 (s), 102.4 (s), 79.0 (s), 74.6 (s), 52.7 (q), 52.5 (q), 52.1 (q), 52.1 (q), 43.7 (d), 41.7 (d), 19.0 (t); UV/Vis (CHCl₃): λ_{abs} (ϵ mol⁻¹dm³cm⁻¹) 250 (42000), 346 (13000)nm; Emission (CHCl₃): λ_{em} 384, 466 nm; MS (FAB): 675 (43) [M+7]⁺, 673 (81) [M+5]⁺, 671 (100) [M+3]⁺, 670 (53) [M+1]⁺; Anal. Calcd for C₂₆H₂₂Cl₆N₂O₆ (671.18): C, 46.53; H, 3.30; N, 4.17; O, 14.40; found: C, 46.34; H, 3.28; N, 3.95; O, 14.79.

(1 α ,2 β ,4 β ,5 α ,8 α ,9 β ,11 β ,12 α)-14,21-diaza-1,5,8,12-tetrachloro-23,23,24,24-tetramethoxy-17,1
8-dinitroheptacyclo[10.10.1.1^{5,8}.0^{2,11}.0^{4,9}.0^{13,22}.0^{15,20}]tetracosane-

13(22),14,16,18,20-pentaene-6,7-dione. Reaction time 30 hours, yield 84 %. M.p. 234-236 °C (decomp); IR (KBr): 3803 (w), 2992 (w), 2952 (m), 2849 (w), 1798 (m), 1771 (s), 1546 (s), 1353 (s), 1194 (s); ¹H NMR (400 MHz, CDCl₃): δ 8.75 (s, 2H), 3.78 (s, 3H), 3.70 (s, 3H), 3.48 (s, 3H), 3.38 (s, 3H), 3.04 (dd, J = 7.2, 4.4 Hz, 2H), 3.80 (dd, J = 7.2, 4.4 Hz, 2H), 2.02 (ddd, J = 13.6, 4.4, 4.0 Hz, 2H), -0.40 (d, J = 13.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 187.3 (s), 157.1 (s), 142.8 (s), 142.8 (s), 127.3 (d), 111.9 (s), 102.4 (s), 78.9 (s), 74.6 (s), 52.8 (q), 52.7 (q), 52.4 (q), 52.1 (q), 43.5 (d), 41.6 (d), 19.1 (t); UV/Vis (CHCl₃): λ_{abs} (ϵ mol⁻¹dm³cm⁻¹) 262 nm (29000); Emission (CHCl₃): λ_{em} 365, 478 nm; MS (FAB): 698 (5) [M+8]⁺, 696 (16) [M+6]⁺, 694 (30) [M+4]⁺, 692 (61) [M+2]⁺, 690 (8) [M]⁺, 136 (100); HRMS (FAB) Calcd for C₂₆H₂₃Cl₄N₄O₁₀ [M+H]⁺: 691.1068; found: 691.1075; Anal. Calcd for C₂₆H₂₂Cl₄N₄O₁₀ (692.29): C, 45.11; H, 3.20; N, 8.09; O, 23.11; found: C, 44.75; H, 2.99; N, 8.51; O, 22.97.

(1 α ,2 β ,4 β ,5 α ,8 α ,9 β ,11 β ,12 α)-14,25-diaza-1,5,8,12-tetrachloro-27,27,28,28-tetramethoxy-
octacyclo[14.10.1.1^{5,8}.0^{2,11}.0^{4,9}.0^{13,26}.0^{15,24}.0^{17,22}]octacosane-13(22),14,16,18,20,22,24-
heptaene-6,7-dione. Reaction time 8 hours, yield 93 %. M.p. 234-235 °C (decomp.); IR (KBr):

3051 (w), 2984 (s), 2951 (s), 2845 (m), 1799 (s), 1771 (s), 1447 (m), 1196 (s); ^1H NMR (400 MHz, CDCl_3): δ 8.75 (s, 2H), 8.12 (dd, $J = 6.4, 3.5$ Hz, 2H), 7.63 (dd, $J = 6.4, 3.5$ Hz, 2H), 3.80 (s, 3H), 3.68 (s, 3H), 3.44 (m, 6H), 2.98 (dd, $J = 7.2, 4.4$ Hz, 2H), 2.78 (dd, $J = 7.2, 4.8$ Hz, 2H), 2.02 (d, $J = 13.6$ Hz, 2H), -0.22 (d, $J = 13.6$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 187.1 (s), 152.3 (s), 138.4 (s), 133.9 (s), 128.5 (d), 128.2 (d), 127.2 (d), 110.8 (s), 102.4 (s), 79.1 (s), 74.8 (s), 52.7 (q), 52.5 (q), 52.1 (q), 52.1 (q), 43.8 (d), 41.8 (d), 19 (t); UV/Vis (CHCl_3): λ_{abs} ($\epsilon \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) 279 (91000), 369 (10000) nm; Emission (CHCl_3): λ_{em} 492 nm; MS (FAB): 658 (1) $[\text{M}+8]^+$, 656 (4) $[\text{M}+6]^+$, 654 (9) $[\text{M}+4]^+$, 652 (11) $[\text{M}+2]^+$, 650 (4) $[\text{M}]^+$, 154 (100); HMRS (FAB) Calcd for $\text{C}_{26}\text{H}_{23}\text{Cl}_6\text{N}_2\text{O}_6$ $[\text{M}+\text{H}]^+$: 651.0623; found: 651.0630.

General procedure for the preparation of unsymmetric syn-bis-quinoxalines C:

Into a solution of the quinoxaline-attached α -diketone **D** (0.50 mmol) in chlorobenzene (12.5 mL) containing a catalytic amount of zinc acetate was added α -phenylenediamine (0.55 mmol) under reflux for hours, monitored by TLC and ^1H NMR. The reaction mixture was filtered to remove salt and the filtrate was concentrated. The residue was purified *via* recrystallization from EtOH/ CHCl_3 (2/1 by vol.) to afford pure adduct.

(1 α ,2 β ,4 β ,5 α ,16 α ,17 β ,19 β ,20 α)-7,14,22,29-tetraaza-1,5,10,11,16,20-hexachloro-31,31,32,32-tetramethoxynonacyclo[18.10.1.1^{5,16}.0^{2,19}.0^{4,17}.0^{6,15}.0^{8,13}.0^{21,30}.0^{23,28}]dotriaconane-6(15),7,9,11,13,21(30),22,24,26,28-decaene. Reaction time 40 hours, yield 93 %. M.p. >300 °C; IR (KBr): 3057 (w), 2981 (w), 2949 (m), 2843 (m), 1473 (m), 1194 (s); ^1H NMR (400 MHz, CDCl_3): δ 7.81 (s, 2H), 7.78 (dd, $J = 6.4, 3.5$ Hz, 2H), 7.66 (dd, $J = 6.4, 3.5$ Hz, 2H), 3.74 (s, 3H), 3.73 (s, 3H), 3.35 (s, 3H), 3.33 (s, 3H), 2.78 (m, 4H), 1.96 (ddd, $J = 13.6, 4.4, 4.0$ Hz, 2H), -1.21 (d, $J = 13.6$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 153.2 (s), 151.8 (s), 141.2 (s), 139.8 (s), 134.2 (s), 129.5 (d), 129.4 (d), 128.7 (d), 111.2 (s), 111.1 (s), 74.7 (s), 74.7 (s), 52.3 (q), 52.3 (q), 52.0 (q), 52.0 (q), 43.0 (d), 42.9 (d), 19.6 (t); UV/Vis (mixture, CHCl_3): λ_{abs} ($\epsilon \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) 243 (52000), 346 (12000) nm; Emission (mixture, CHCl_3): λ_{em} 398 nm; MS (FAB): 748 (4) $[\text{M}+8]^+$, 746 (4) $[\text{M}+6]^+$, 744 (3) $[\text{M}+4]^+$, 742 (4) $[\text{M}+2]^+$, 154 (100); HRMS (FAB) Calcd for $\text{C}_{32}\text{H}_{27}\text{Cl}_6\text{N}_4\text{O}_4$ $[\text{M}+\text{H}]^+$: 741.0164; found: 741.0172; Anal. Calcd for $\text{C}_{32}\text{H}_{26}\text{Cl}_6\text{N}_4\text{O}_4$ (743.29): C, 51.51; H, 3.53; N, 7.54; O, 8.61; found: C, 51.13; H, 3.83; N, 7.39; O, 8.59.

(1 α ,2 β ,4 β ,5 α ,20 α ,21 β ,23 β ,24 α)-7,18,26,33-tetraaza-1,5,20,24,29,30-hexachloro-35,35,46,46-

tetramethoxydecacyclo[22.10.1.1^{5,20}.0^{2,23}.0^{4,21}.0^{6,19}.0^{8,17}.0^{10,15}.0^{25,34}.0^{27,32}]hexatriacontane-6(19),7,9,11,13,15,17,25(38),26,28,30,32,34,36-dodecaene. Reaction

time 45 hours, yield 94 %. M.p. >300 °C; IR (KBr): 3057 (w), 2981 (w), 2949 (m), 2843 (m), 1474 (m), 1195 (s); ¹H NMR (400 MHz, CDCl₃): δ 8.36 (s, 2H), 8.06 (dd, *J* = 6.4, 3.5 Hz, 2H), 7.65 (dd, *J* = 6.4, 3.5 Hz, 2H), 7.65 (s, 2H), 3.76 (s, 3H), 3.72 (s, 3H), 3.63 (s, 3H), 3.31 (s, 3H), 2.91 (m, 4H), 2.02 (ddd, *J* = 13.6, 4.4, 4.0 Hz, 2H), -0.97 (d, *J* = 13.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 153.1 (s), 152.5 (s), 139.7 (s), 137.4 (s), 134.0 (s), 133.3 (s), 128.8 (d), 128.5 (d), 127.6 (d), 127.2 (d), 111.2 (s), 110.3 (s), 74.9 (s), 74.8 (s), 52.4 (q), 52.3 (q), 52.0 (q), 52.0 (q), 43.1 (d), 43.0 (d), 19.7 (t); UV/Vis (mixture, CHCl₃): λ_{abs} (ε mol⁻¹dm³cm⁻¹) 253(68000), 280 (81000)nm; Emission (mixture, CHCl₃): λ_{em} 488 nm.

36

(1α,2β,4β,5α,16α,17β,19β,20α)-7,14,22,29-tetraaza-1,5,16,20-tetrachloro-31,31,32,32-tetramethoxy-10,11-dinitrononacyclo[18.10.1.1^{5,16}.0^{2,19}.0^{4,17}.0^{6,15}.0^{8,13}.0^{21,30}.0^{23,28}]dotria-conane-6(15),7,9,11,13,21(30),22,24,26,28-decaene.

Reaction time 27 hours, yield 80 %. M.p. >300 °C; IR (KBr): 3078 (w), 2979 (m), 2952 (s), 1546 (s), 1354 (s), 1194 (s); ¹H NMR (400 MHz, CDCl₃): δ 8.26 (s, 2H), 7.81 (dd, *J* = 6.4, 3.5 Hz, 2H), 7.58 (dd, *J* = 6.4, 3.5 Hz, 4H), 3.74 (s, 6H), 3.35 (s, 3H), 3.33 (s, 3H), 2.92 (m, 4H), 2.02 (d, *J* = 13.6 Hz, 2H), -1.24 (d, *J* = 13.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 157.4 (s), 152.0 (s), 142.0 (s), 141.7 (s), 141.1 (s), 130.0 (d), 128.6 (d), 126.4 (d), 111.3 (s), 111.2 (s), 74.7 (s), 74.6 (s), 52.5 (q), 52.4 (q), 52.3 (q), 52.0 (q), 42.9 (d), 42.7 (d), 19.8 (t); UV/Vis (mixture, CHCl₃): λ_{abs} (ε mol⁻¹dm³cm⁻¹) 244 (46000), 316 (11000)nm; Emission (mixture, CHCl₃): λ_{em} 361 nm; MS (FAB): 770 (4) [M+8]⁺, 768 (6) [M+6]⁺, 766 (9) [M+4]⁺, 764 (5) [M+2]⁺, 154 (100); HRMS (FAB) Calcd for C₃₂H₂₇Cl₄N₆O₈ [M+H]⁺: 763.0645; found: 763.0648; Anal. Calcd for C₃₂H₂₆Cl₄N₆O₈ (764.40): C, 50.18; H, 3.53; N, 10.99; O, 16.74; found: C, 49.81; H, 3.90; N, 11.15; O, 16.72.

37

(1α,2β,4β,5α,20α,21β,23β,24α)-7,18,26,33-tetraaza-1,5,20,24,29,30-hexachloro-35,35,46,46-tetramethoxy-29,30-dinitrodecacyclo[22.10.1.1^{5,20}.0^{2,23}.0^{4,21}.0^{6,19}.0^{8,17}.0^{10,15}.0^{25,34}.0^{27,32}]hexatriacontane-6(19),7,9,11,13,15,17,25(38),26,28,30,32,34,36-dodeca-ene. Reaction time 37 hours, yield 92 %. M.p. >300 °C; IR (KBr): 3079 (w), 2979 (m), 2952 (s), 1546 (s), 1354 (s), 1194 (s); ¹H NMR (400 MHz, CDCl₃): δ 8.39 (s, 2H), 8.12 (s, 2H), 8.01 (dd, *J* = 6.4, 3.5 Hz, 4H), 7.64 (dd, *J* = 6.4, 3.5

38

Hz, 4H), 3.77 (s, 3H), 3.74 (s, 3H), 3.38 (s, 3H), 3.30 (s, 3H), 3.00-2.93 (m, 4H), 2.07 (d, $J = 13.6$ Hz, 2H), -0.99 (d, $J = 13.6$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 157.3 (s), 152.2 (s), 141.6 (s), 140.7 (s), 137.3 (s), 133.1 (s), 128.1 (d), 128.0 (d), 127.1 (d), 126.1 (d), 111.3 (s), 110.3 (d), 74.7 (s), 74.6 (s), 52.5 (q), 52.2 (q), 52.2 (q), 52.0 (q), 42.9 (d), 42.8 (d), 19.8 (t); UV/Vis (mixture, CHCl_3): λ_{abs} ($\epsilon \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$) 269 nm (45000); Emission (mixture, CHCl_3): λ_{em} 553 nm.

(1 α ,2 β ,4 β ,5 α ,20 α ,21 β ,23 β ,24 α)-7,18,26,33-tetraaza-1,5,20,24-tetrachloro-35,35,46,46-tetramethoxydecacyclo[22.10.1.1^{5,20}.0^{2,23}.0^{4,21}.0^{6,19}.0^{8,17}.0^{10,15}.0^{25,34}.0^{27,32}]hexatriacontane-6(19),7,9,11,13,15,

17,25(38),26,28,30,32,34,36-dodecaene. Reaction time 35 hours, yield 86 %. M.p. >300 °C;; IR (KBr): 3056 (w), 2981 (w), 2947 (m), 2843 (w), 1456 (m), 1189 (s); ^1H NMR (400 MHz, CDCl_3): δ 8.26 (s, 2H), 8.02 (dd, $J = 6.4, 3.5$ Hz, 2H), 7.68 (dd, $J = 6.4, 3.5$ Hz, 2H), 7.42 (dd, $J = 6.4, 3.5$ Hz, 2H), 6.55 (dd, $J = 6.4, 3.5$ Hz, 2H), 3.75 (s, 3H), 3.72 (s, 3H), 3.38 (s, 3H), 3.31 (s, 3H), 2.91-2.87 (m, 4H), 1.99 (ddd, $J = 13.6, 4.4, 4.0$ Hz, 2H), -1.02 (d, $J = 13.6$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 152.6 (s), 151.6 (s), 140.8 (s), 137.5 (s), 133.4 (s), 128.6 (d), 128.6 (d), 127.9 (d), 127.4 (s), 126.8 (d), 111.2 (s), 110.3 (s), 74.8 (s), 74.8 (s), 52.3 (q), 52.2 (q), 52.0 (q), 51.9 (q), 43.1 (d), 43.0 (d), 19.5 (t); UV/Vis (mixture, CHCl_3): λ_{abs} ($\epsilon \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$) 249 (45000), 279 (67000), 325 (7000), 333 (7000), 351 (5000), 369 (8000)nm; Emission (mixture, CHCl_3): λ_{em} 479 nm; MS (FAB): 730 (5) $[\text{M}+8]^+$, 728 (40) $[\text{M}+6]^+$, 726 (68) $[\text{M}+4]^+$, 725 (100) $[\text{M}+\text{H}+2]^+$, 724 (61) $[\text{M}+2]^+$, 673 (22) $[\text{M}]^+$; HRMS (FAB) Calcd for $\text{C}_{36}\text{H}_{31}\text{Cl}_4\text{N}_4\text{O}_4$ $[\text{M}+\text{H}]^+$: 723.1089; found: 723.1097.

Figure 1. UV/Vis spectra of Syn-bis-quinoxaline **17-26** in CHCl_3 ; $c = 1.5 \times 10^{-5} \text{ M}$.

Figure 2. Fluorescence emission spectra of Syn-bis-quinoxaline **17-24** in CHCl_3 ; $c = 1.0 \times 10^{-5} \text{ M}$; $\lambda_{\text{ex}} = \text{absorption } \lambda_{\text{max}}$. The intensity was normalized.

Figure 3. UV/Vis spectra of Syn-bis-quinoxaline **27**, **28**, and **42** in CHCl_3 ; $c = 1.0 \times 10^{-5}$ M.

Figure 4. Fluorescence spectra of bis-benzo-quinoxalines **27**, **28**, and **42** in CHCl_3 (solid line) and DMSO (dash line); $c = 1.0 \times 10^{-5}$ M; λ_{ex} = absorption λ_{max} . The intensity was normalized.

Figure 5. UV/Vis spectra of the Quinoxaline-attached α -diketone **29-33** in CHCl_3 ; $c = 1.0 \times 10^{-5}$ M.

Figure 6. Fluorescence emission spectra of Quinoxaline-attached α -diketone **29-32** in CHCl_3 ; $c = 1.0 \times 10^{-5}$ M; λ_{ex} = absorption λ_{max} . The intensity was normalized.

Figure 7. UV/Vis spectra of the Quinoxaline-attached α -diketone **34** in CHCl_3 ; $c = 1.0 \times 10^{-5}$ M.

Figure 8. Fluorescence emission spectra of the Quinoxaline-attached α -diketone **34** in CHCl_3 (solid line) and DMSO (dash line); $c = 1.0 \times 10^{-5}$ M; λ_{ex} = absorption λ_{max} . The intensity was normalized.

Figure 9. UV/Vis spectra of Unsymmetric Syn-bis-quinoxaline **36**, **38**, and **39** in CHCl_3 ; $c = 1.0 \times 10^{-5} \text{ M}$.

Figure 10. Fluorescence emission spectra of unsymmetrical bis-quinoxalines **36**, **38**, and **39** in CHCl_3 (solid line) and DMSO (dash line); $c = 1.0 \times 10^{-5} \text{ M}$; $\lambda_{\text{ex}} = \text{absorption } \lambda_{\text{max}}$. The intensity was normalized.

Figure 11. Molecular structure of Syn-bis-quinoxalines **17**. Thermal ellipsoids are drawn at 30% probability