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Quinoxaline-based U-shaped septuple-bridged [7,7]orthocyclophanes: synthesis, solid-state structure, and self-assembly

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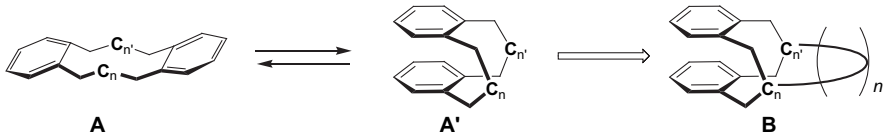
ABSTRACT

We report a three-step synthesis of 12 septuple-bridged [7,7]orthocyclophanes **11** comprising (i) two quinoxaline-based sidewalls and (ii) a linker built-in with a succinimide ring that carries phenyl, *p*-methoxyphenyl, *p*-hydroxyphenyl, or *p*-methoxybenzyl appendants. The synthesis began from the Diels–Alder adduct of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (**1**) and succinimide ring-fused dioxatetracyclodecadiene **9**, followed by ruthenium-promoted oxidation of dichloroetheno-bridges in the adduct to generate a bis-α-diketone, which was then condensed with an arene-1,2-diamine to construct sidewalls (phane parts), furnishing U-shaped septuple-bridged [7,7]orthocyclophanes **11** embedding quinoxaline, dimethylquinoxaline, or benzoquinoxaline rings. Concentration-variant ^{1}H NMR spectra of *N*-*p*-methoxybenzyl substituted orthocyclophanes (**11zd**, **11xd**, and **11yd**) and single-crystal structures of four orthocyclophanes (**11xa**, **11yd**, **11zb**, and **11zd**) revealed that the U-shaped septuple-bridged [7,7]orthocyclophanes **11** have a tendency of self-assembly, forming V-shaped dimeric entities driven chiefly by intermolecular π–π stacking interaction in both solid state and solution of high concentration.

1. Introduction

[*n*,*n*′]Orthocyclophanes are polycyclic molecules consisting of aromatic units (typically benzene rings) connected between the *ortho* positions of the aromatic rings by aliphatic chains of *n*- and *n*′-atom length. Compared with the various *meta*,*meta*- and *para*,*para*-[*n*,*n*′]cyclophanes,[1] they are less strained and have the possibility of existing in two different conformations, in which the aromatic units are in antiparallel (*anti*-periplanar, **A**) or parallel fashion (*syn*-periplanar, **A**′).[2] The aromatic rings could be forced to align face-to-face in proximity by means of bridge(s) across the aliphatic chains. The bridged [*n*,*n*′]orthocyclophanes (**B**) thereby structured acquire a rigid U-shape framework like a clip or a tweezer having concave-convex topology. Notable examples are systems derived from Troger's base,[3] Kagan's ether,[4] glycoluril,[5] 'byobuene',[6] and others that are linked by a rigid polycyclic spacer.[7] With the attachment of specially designed functional groups or fluorophores to the aromatic rings, they afford opportunity to demonstrate the formation of host–guest complex[8,9] and self-assembled dimeric entity[10] via the processes manipulated by weak but specific noncovalent intermolecular interactions, to explore potential application as sensing systems,[11] and for investigating intramolecular long-range electron/energy transfer phenomena between the electronically coupled donor and acceptor chromophores.[12]



Recently, we developed an efficient three-step synthetic approach to the U-shaped multi-bridged [*n*,*n*′]orthocyclophanes containing various quinoxaline rings with the generic structure **E**, via the process illustrated in Scheme 1.[13] This process consists of three fundamental operations: (1) the Diels–Alder reaction of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (TDCp, **1**)[14] with a bis-dienophile to

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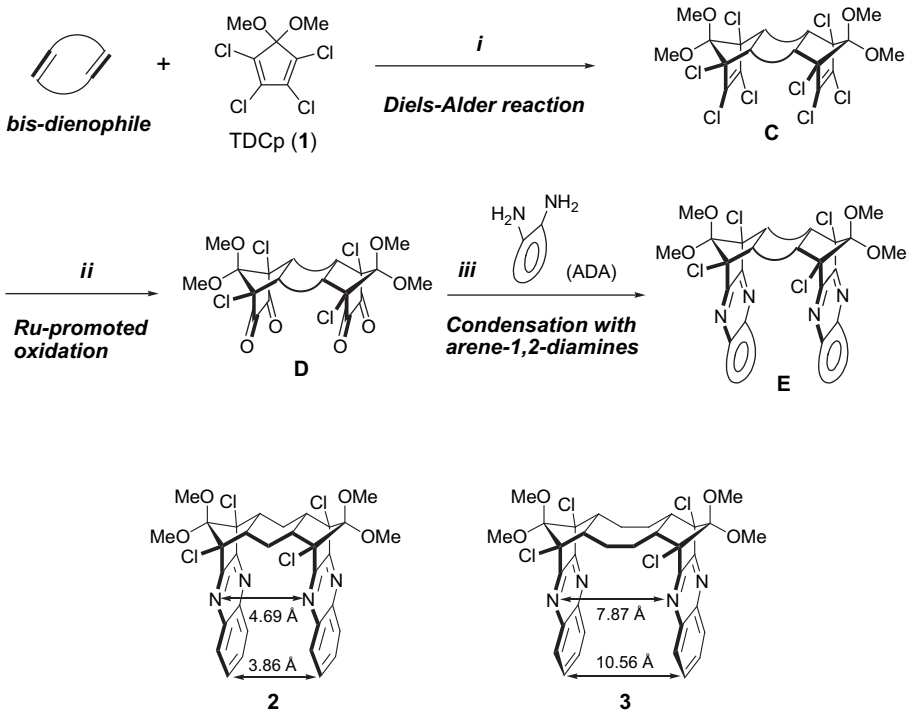
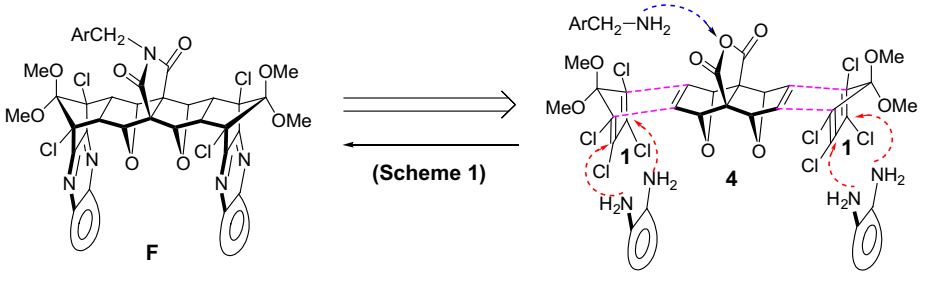


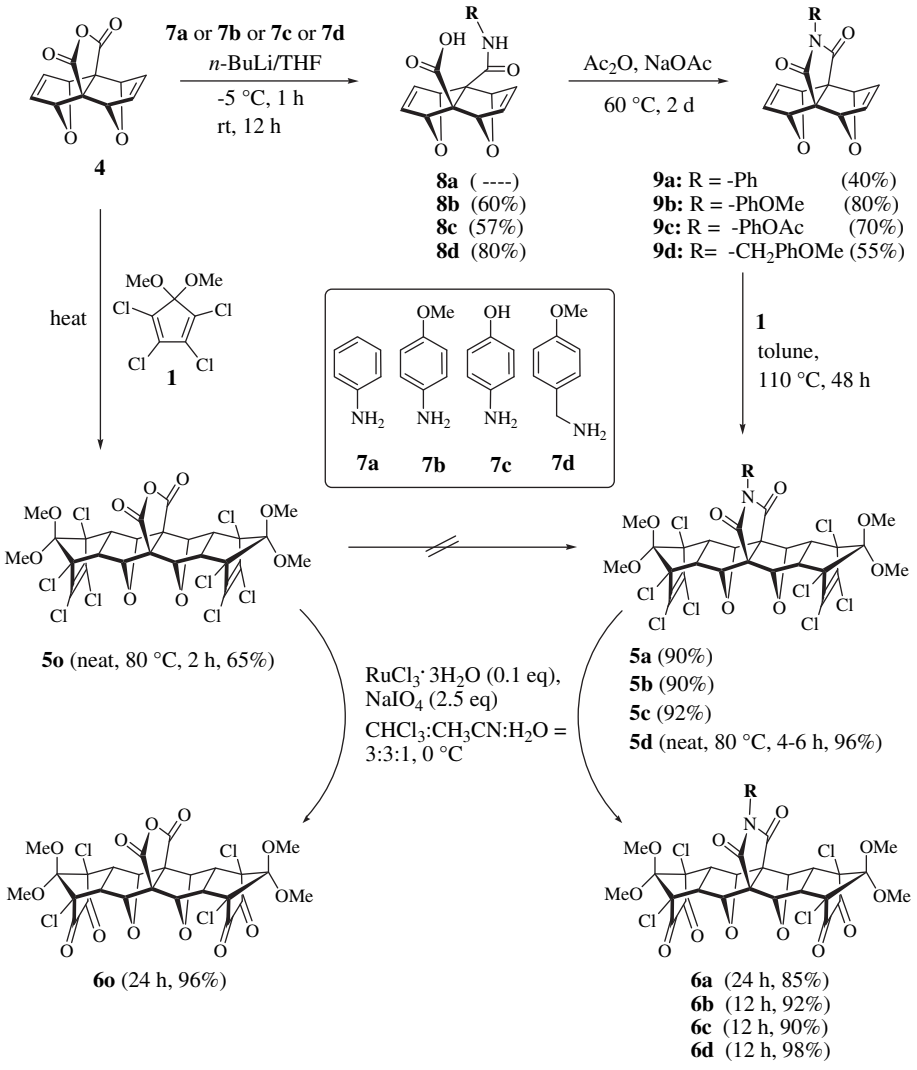
Scheme 1. Synthetic strategy for the construction of U-shaped multi-bridged orthocyclophanes.

construct bis-adduct **C** as the central scaffold, (2) the conversion of dichloroetheno-bridges in **C** by ruthenium-promoted oxidation using Khan's protocol[15] to generate bis-α-diketone **D**, followed by (3) the construction of sidewalls (phane parts) by the condensation of bis-α-diketone **D** with an arene-1,2-diamine (ADA) to produce the U-shaped [*n*,*n*′]orthocyclophanes **E** embedding quinoxaline-based aromatic rings. The practicality and efficacy of the synthetic strategy illustrated in Scheme 1 was demonstrated by the synthetic implementation of the U-shaped quadruple-bridged [5,5]orthocyclophanes **2**, [6,6]orthocyclophane **3**, and their derivatives from the Diels–Alder adducts of TDCp with 1,4-cyclohexadiene and 1,5-cyclooctadiene, respectively.[13,16]

As revealed by the X-ray single-crystal structure, the pair of face-to-face quinoxaline rings in **2** stretches out from the boat cyclohexane-intercalated scaffold in an inward (converging) fashion with transannular distances (d_{NN}=4.69 Å, d_{CC}=3.86 Å), permissible for significant intramolecular excimer interaction between quinoxalinyl chromophores.[13] On the other hand, the molecular structure of **3** exhibits two quinoxaline rings facing each other and suspending from the boatlike cyclooctane-intercalated scaffold in an outward (diverging) style with distances (d_{NN}=7.87 Å, d_{CC}=10.56 Å) between quinoxalinyl chromophores, too far apart to interact with each other and inappropriate to develop stable host–guest complexes.

We were then prompted to alter the linker (bis-dienophile) and worked on the synthesis of the septuple-bridged [7,7]orthocyclophanes with generic formula **F** that contains face-to-face aligned quinoxaline rings and *N*-arylsuccinimide group on the opposite side of the molecular framework platform, using dioxatetracyclic bis-alkene anhydride **4**[17] as an entry point. We envisaged that the cycloaddition of TDCp (**1**) onto **4** should follow the same stereoselectivity exhibited by that of cyclopentadiene and 7-oxanorbornenes,[17] and is predictable based on the consideration of steric hindrance put forth by the anhydride moiety of **4**. In a sense, the double Diels–Alder adduct thus formed is structurally extraordinary. Both sides of the molecular framework carry functional groups suitable for further elaboration. One side (top) is suitable for effecting the imidization of dicarboxylic anhydride moiety with primary amines to furnish dicarboximides, and the other side (bottom) for transforming the dihaloetheno-bridges to the corresponding α-dioxoetheno-bridges by ruthenium-promoted oxidation[15] (Scheme 1) to lay a concrete way toward the U-shaped septuple-bridged [7,7]orthocyclophanes **F** of our interest. Molecular modeling predicted that [7,7]orthocyclophanes **F** thereby constructed by the condensation of derived bis-α-diketones with various arene-1,2-diamines could have the sidewalls aligned in parallel fashion with transannular distance of about 7.7 Å, more apt for the formation of host–guest complexes by clipping via arene–arene interactions.[18] This paper describes the synthesis and self-assembly of the U-shaped septuple-bridged [7,7]orthocyclophanes driven chiefly by π–π stacking interaction involving quinoxaline-based aromatic rings.





Scheme 2. Synthesis of *syn*-bis-α-diketonic platform molecules **6**.

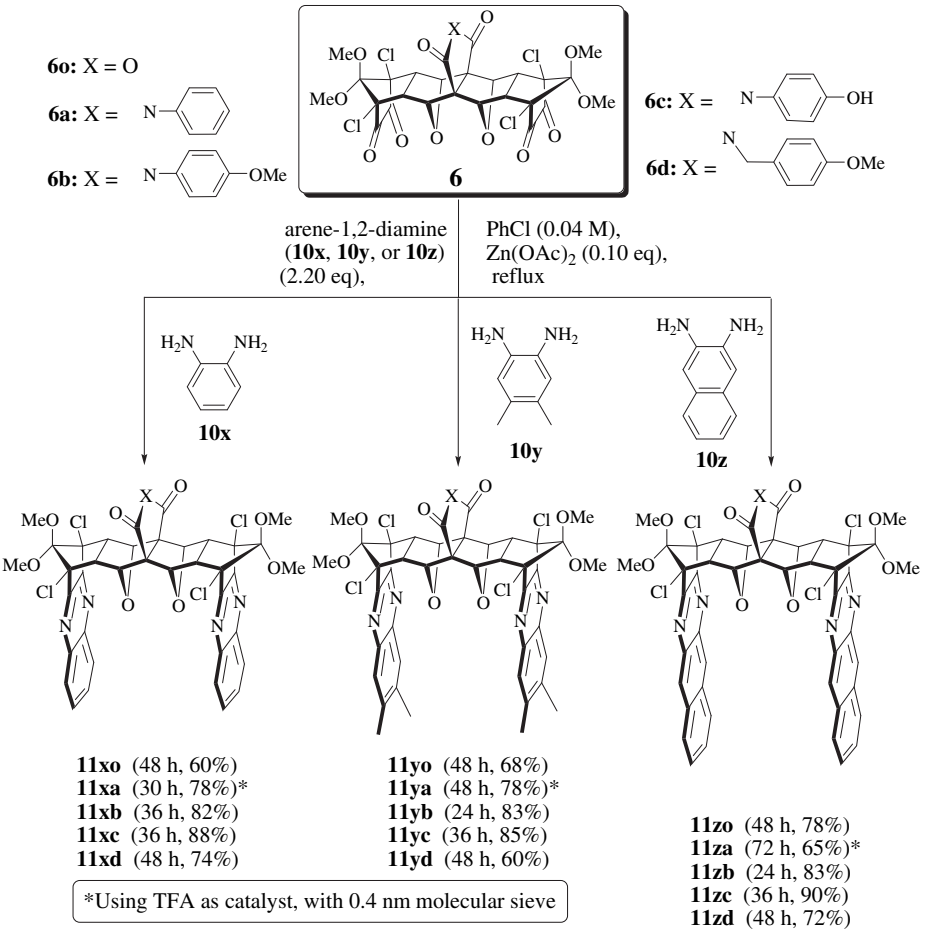
2. Results and discussion

2.1. Synthesis

The dioxatetracyclic bis-alkene anhydride **4** was prepared from the corresponding bis-adduct of furan and acetylene dicarboxylic acid[19] by treatment with oxalyl chloride in refluxing CH_2Cl_2.[17] As shown in Scheme 2, heating anhydride **4** with TDCp (**1**) under neat condition at 80 °C for 2 h afforded bis-adduct **5o** in 65% yield, which was converted to bis-α-diketone **6o** in almost quantitative yield (96%) by following essentially the ruthenium-promoted oxidation procedure reported by Khan et al. [$RuCl_3 \cdot 3H_2O$ (0.1 equiv), $NaIO_4$ (2.5 equiv), $CHCl_3/CH_3CN/H_2O$=3:3:1, 0 °C, 12 h].[15] The bis-adduct **5o** was found to be inert to the condensation with primary amines to give the corresponding *N*-substituted succinimides, even under forcing conditions. Apparently, the anhydride moiety in **5o** is shielded by the hydrogen atoms at ring junctions. Consequently, the synthesis of succinimide series of septuple-bridged [7,7]orthocyclophanes required recourse to the conversion of anhydride **4** to the succinimides **9** prior to performing the Diels–Alder reaction with TDCp.

The conversion was achieved in two steps by reaction with primary amine [aniline (**7a**), 4-methoxybenzenamine (**7b**), 4-aminophenol (**7c**), or *p*-methoxybenzylamine (**7d**)] in THF in the presence of *n*-BuLi and cyclization of the resultant amic acid **8** with sodium acetate in acetic anhydride at 60 °C.[17] Regrettably, the overall yields of succinimides **9** from **4** were rather low (40–50%), probably due to the propensity of amic acids **8** to undergo retro-Diels–Alder fragmentation. The reaction of **4** with 4-aminophenol (**7c**) gave *N*-*p*-acetoxyphenylsuccinimide **9c** resulting from acetylation of phenolic hydroxyl group. The succinimide **9a–d** thereby obtained were subjected to the Diels–Alder reaction with TDCp affording bis-adducts **5a–d** in the yields of 90–96%. As expected, the cycloaddition of TDCp onto the π-bonds of **9a–d** occurred in high yield and stereoselectivity to furnish the U-shaped cavity molecules **5a–d**, which were then oxidized by using Khan's procedure to deliver the corresponding bis-α-diketones **6a–d** in yields of 85–98%.

We have previously demonstrated that quinoxaline sidewalls could be installed cleanly in high yields by performing the reaction of bis-α-diketone with arene-1,2-diamines (ADA) in PhCl at refluxing temperature and in the presence of $Zn(OAc)_2$ as a catalyst.[13] As shown in Scheme 3, applying the same procedure to the condensation reactions of bis-α-diketone **6o** with ADA [benzene-1,2-diamine (**10x**), 4,5-dimethylbenzene-1,2-diamine (**10y**), and naphthalene-2,3-diamine (**10z**)], the corresponding septuple-bridged [7,7]orthocyclophanes containing quinoxaline (**11xo**), dimethylquinoxaline (**11yo**), and benzoquinoxaline rings (**11zo**) were realized in yields of 60–78%. When bis-α-diketones **6a–d** were



Scheme 3. Synthesis of U-shaped septuple-bridged [7,7]orthocyclophanes 11 from *syn*-bis-α-diketones **6**.

allowed to react with ADA (**10x**, **10y**, and **10z**) in refluxing PhCl in the presence of catalytic amount of $Zn(OAc)_2$ for 1–2 days, the desired septuple-bridged [7,7]orthocyclophanes **11**'s were also obtained in good yields (60–90%). In the case of bis-α-diketone **6a**, the condensation reactions were also performed by using TFA as catalyst and molecular sieve (0.4 nm) as water scavenger to furnish the corresponding orthocyclophanes **11xa**, **11ya**, and **11za** in good yields. The acetyl group at **6c** inherent from **9c** was lost during the $Zn(OAc)_2$-catalyzed condensation reactions, producing *N*-*p*-hydroxyphenyl orthocyclophanes **11xc**, **11yc**, and **11zc**, which were converted to the corresponding acetates for supplementary structural characterization. All the U-shaped septuple-bridged [7,7]orthocyclophanes and their respective precursor molecules gave satisfactory elemental analyses or HRMS data and were properly characterized by their $^1H/^{13}C$ NMR, IR, and MS spectral analyses (Experimental section).

2.2. ^{1}H NMR spectral study

The U-shaped septuple-bridged [7,7]orthocyclophanes **11** exhibit conformational rigidity and C_{2v} symmetry-reflected ^{1}H NMR spectra. The assignments of the absorption signals for the protons were made using intensity, chemical shift, and splitting pattern, and in some cases further supported by COSY and HMQC experiments. At the onset we recorded the room-temperature ^{1}H NMR spectra of **11zd** at various concentrations in $CDCl_3$. As shown in Figure 1a, when the concentration was gradually increasing from 5.0×10^{-4} M to 1.0×10^{-1} M, the absorption signals of H_e, H_f, and H_g at the benzoquinoxaline ring displayed steady shift toward higher magnetic field, up to a total of about 1.05, 0.95, and 0.52 ppm, respectively. Particularly, the protons located closer to the nitrogen atoms of benzoquinoxaline ring showed larger shift (H_e>H_f>H_g). Whereas the methine protons(H_b), and protons of *N*-*p*-methoxybenzyl appendant (H_c and H_d) remained essentially unchanged, a downfield movement was observed for the oxa-bridgehead methine H_a (0.33 ppm). This observation implied the occurrence of the concentration-dependent molecular self-assembly and prompted us to perform the same experiment on **11xd** and **11yd** (Fig. 1b and c, respectively). Similarly, upfield shifts of the quinoxaline ring protons (H_e/H_f) and downfield shift of the oxa-bridgehead methine proton (H_a) were observed for **11xd**, albeit in much less magnitude (0.18/0.16 ppm and 0.06 ppm, respectively), in the concentration range of 5.0×10^{-4} M to 3.0×10^{-2}. Similar phenomenon was observed for **11yd** in the concentration range of 3.0×10^{-4} M to 3.0×10^{-2}, which showed upfield shifts of the aromatic H_e (0.28 ppm) and methyl H_f (0.23 ppm) at quinoxaline ring and downfield shift of the oxa-bridgehead H_a (0.11 ppm).[20]

The intermolecular π–π stacking interaction plays a fundamental role in stabilizing the self-assembled supramolecular structures of aromatic ring-containing compounds.[18] For the U-shaped orthocyclophanes, intermolecular π–π stacking interaction could conceivably lead to the formation of dimeric entities by simultaneous penetration of the aromatic sidewalls of two orthocyclophane molecules into the opposing U-shaped cleft (i.e., reciprocal clipping) by the type of either orthogonal (**G**) or antiparallel (**H**) manner, as shown schematically in Figure 2. As an alternative, they can assemble in line-up fashion without reciprocal

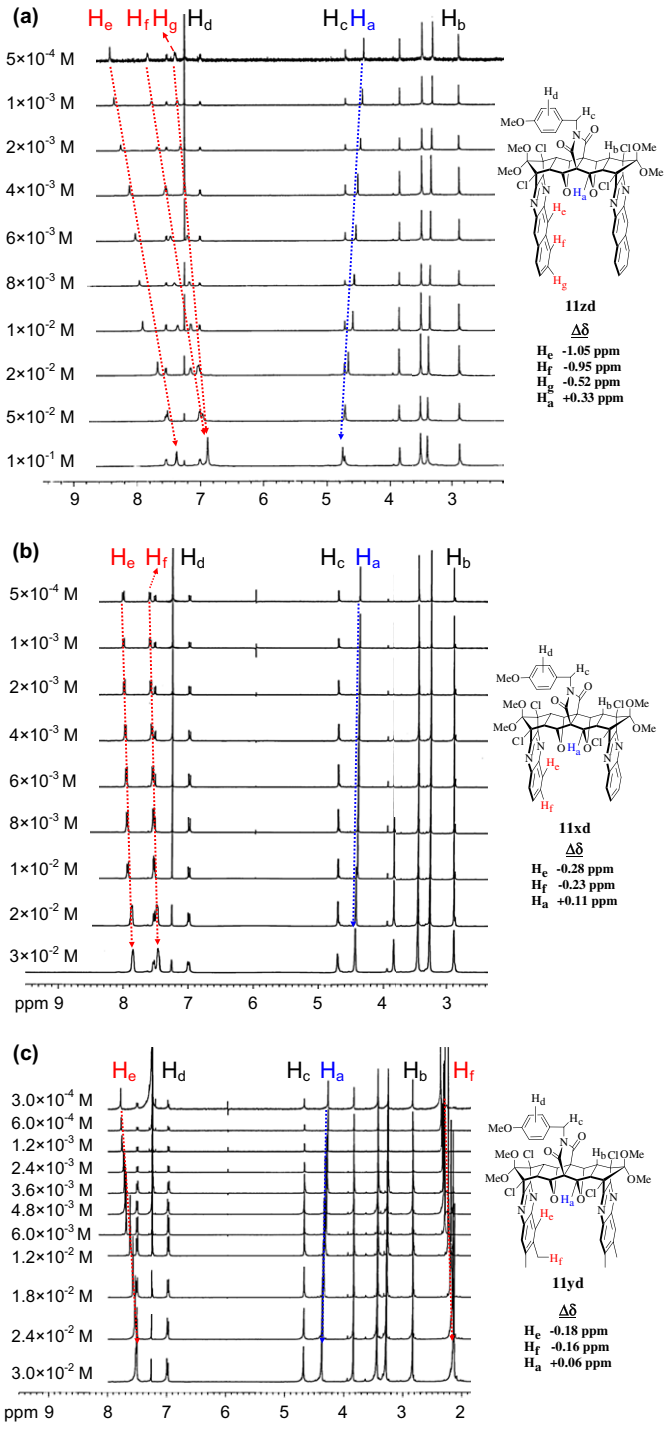


Figure 1. Concentration-variant ^{1}H NMR spectra in $CDCl_3$. (a) **11zd** (500 MHz), (b) **11xd** (400 MHz), (c) **11yd** (400 MHz).

clipping to form dimeric (***I***/***J***) and polymeric entities. The observed concentration-dependent chemical shifts behavior shown in Figure 1 implied that in solution the U-shaped orthocyclophanes **11** could self-assemble to form dimeric entities and coexist in equilibrium with their respective monomers, when the concentration was increasing. The changing trend of chemical shifts suggested that they were more likely to assemble by reciprocal clipping in orthogonal (**G**) or antiparallel (**H**) manner.[13,21] The speculation was supported by examination of the crystal structures of [7,7]orthocyclophanes **11xa**, **11yd**, **11zb**, and **11zd** described in the next section.

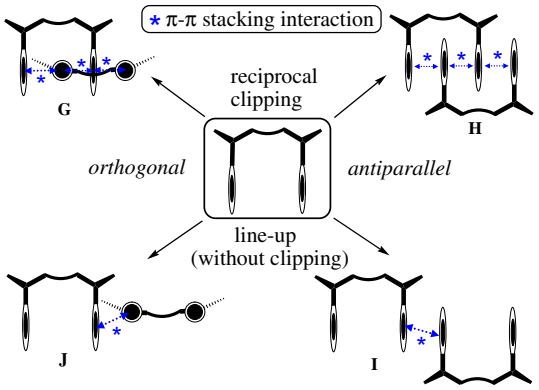


Figure 2. Schematic representations of the possible ways for the U-shaped orthocyclophanes to form dimers driven by π–π stacking interaction.

2.3. X-ray crystal structural study

Among the septuple-bridged [7,7]orthocyclophanes **11** synthesized, we were able to obtain single crystals of **11xa**, **11yd**, **11zb**, and **11zd** that were suitable for room-temperature X-ray crystal structure determination by recrystallization from solvent system of ethanol–chloroform.[22] The ORTEP plots of their X-ray crystal structures are depicted in Figure 3 and the tables for crystal data/structure refinement are provided in Table 1. Table 2 lists some selected parameters from the X-ray crystal structures of **11xa**, **11yd**, **11zb**, and **11zd**, which describe the structure and packing motifs. Probably due to steric constrain resulting from reciprocal clipping to form dimeric entity in the crystal packing, two conformations with different mean interplanar distances were noted for the crystal structure of **11yd**, **11zb**, and **11zd**. Unlike the crystal structures of **2** and **3**,[13] the pair of heteroaromatic rings are stretching out from the rigid intercalator scaffold in almost parallel (*syn*-periplanar) manner (Fig. 3), as indicated by the mean interatomic distances between nitrogen atoms (d_{NN}) and end carbon atoms (d_{CC}), which are nearly equal (<0.5 Å). On the other hand, **11xa** exists in one conformation and displays two quinoxaline rings stretching out in a slightly diverging style (d_{CC}–d_{NN}=~1.08 Å) in the crystal structure. In the rotation-constrained solid state, the phenyl-substituted succinimides **11xa** and **11zb** displayed dihedral angles between the planes of phenyl and imide rings (C_{Ar}–C_{Ar}–N–$C_{C=O}$) by 72.9° and 51.9°/66.5°, respectively (Table 2). As shown in Figure 3, the *p*-methoxyphenyl ring in succinimides **11yd** and **11zd** is inclined alongside, rather than vertically, to the molecular framework. This alignment probably benefits from the intramolecular CH–π interactions[23] of phenyl ring with the polarized C–H bonds of methoxy group at the acetal carbon atom, indicated by short $OCH_3\cdots C_{ph}$ distances (Table 2).

All the orthocyclophanes (**11xa**, **11yd**, **11zb**, and **11zd**) existed as self-assembly dimeric structures in the crystal. As shown in Figure 4, the first salient feature is that the dimeric structure is resulted from simultaneous penetration of the aromatic sidewalls of two orthocyclophane molecules into the opposing U-shaped cleft (i.e., reciprocal clipping) by the type resembling **G** depicted in Figure 2. The molecular skeletons of orthocyclophane in the dimeric structure of **11xa**, **11zb**, **11yd**, and **11zd** are oriented in V-shape by a clipping angle of about 45°, 85°, 81°, and 75°, respectively (Fig. 4, side-view). The mean planes of their heteroaromatic rings are separated by 3.68/5.05 Å, 3.82/3.56 Å, 3.95/4.06 Å, and 3.70/3.50 Å, respectively (Fig. 4, face-view, Table 2), indicating that these aromatic rings benefit from the direct face-to-face π–π stacking interactions in the crystal.[18,24] The π,π interaction appears to be most efficient for orthocyclophanes **11zb** and **11zd**, in which the estimated mutual cover area of benzoquinoxaline rings is about 70% (Fig. 4b and d, side-view). The π,π

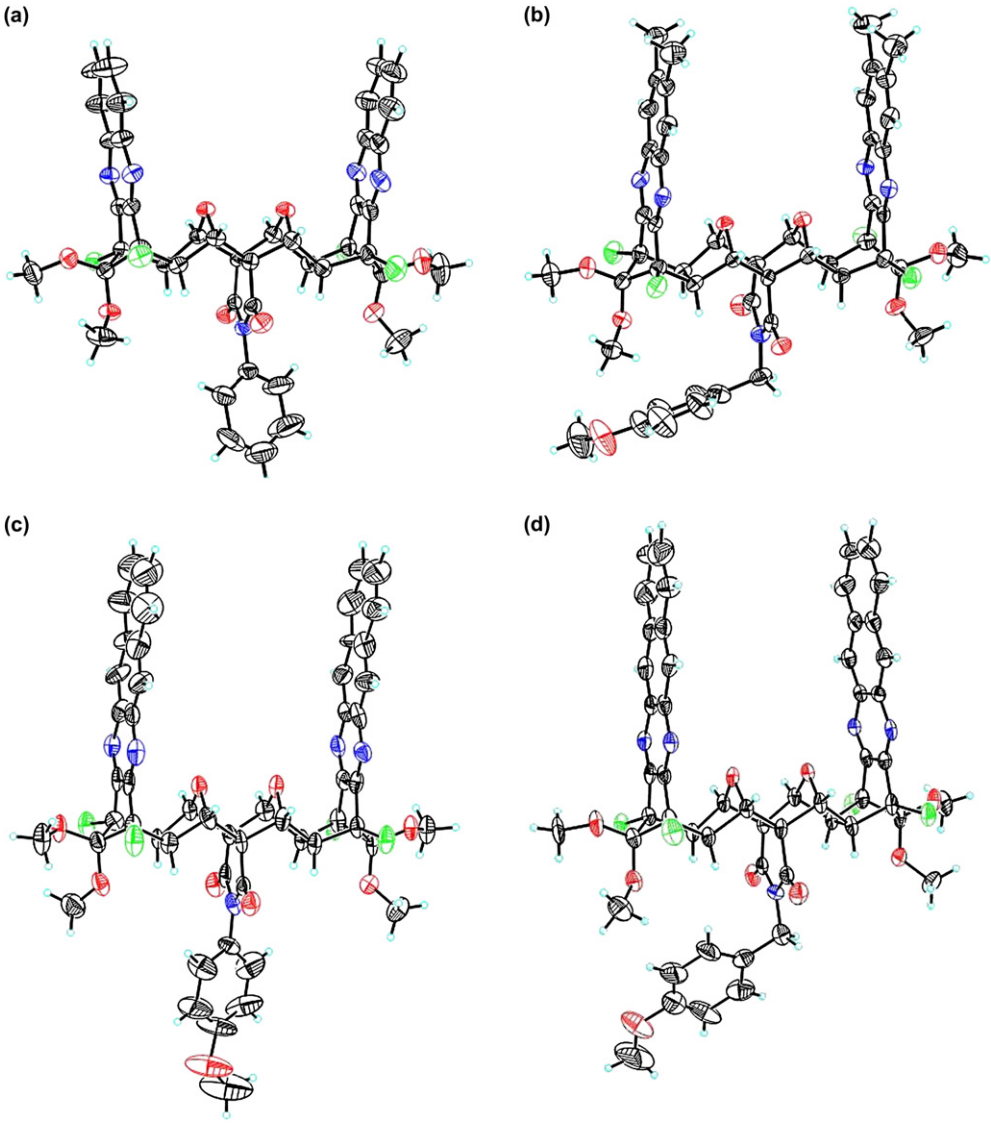


Figure 3. The ORTEP plots of X-ray crystal structures. (a) **11xa**, (b) **11yd**, (c) **11zb**, and (d) **11zd**. Color coding: C, black; H, cyan; N, blue; O, red; Cl, green.

interaction in dimeric **11xa** is expected to be much weaker, because the quinoxaline rings are aligned in an offset parallel geometry (Fig. 4a). In the case of **11yd**, the quinoxaline rings have mutual cover area of about 50% for π,π interaction (Fig. 4c, side-view), which is apparently assisted by the van der Waals interaction of dimethyl substituents to provide additional driving force for effective self-assembly.[18,25] Further examination of the packing motifs in the dimeric structures of **11xa**, **11zb**, **11yd**, and **11zd** interestingly revealed that nitrogen atom of the sandwiched heteroaromatic ring is located close to the hydrogen atoms at two oxa-bridgeheads with H···N distances in the range of 2.65–3.68 Å and H···N···H angles of 56.7–71.5° (Table 2) to exert double O–H···N_{Ar}···H–O hydrogen bonding interactions.[26] The dimeric structures of **11yd**, **11zb**, and **11zd** are additionally stabilized by C–H···N interactions using nitrogen atom of the external heteroaromatic rings and the polarized C–H bonds of one methoxy group of the intercalator, as suggested by short OCH_3···N_{Ar} distances (2.71–3.36 Å, Table 2).[26] We attribute the preference of forming dimeric structure by the type of V-shaped arrangement shown in Figure 4 to these extra intradimeric interactions (see also Fig. 5).

The fact that the U-shaped orthocyclophanes **11** could undergo dimerization in the crystal driven most significantly by π–π stacking interactions evidently echoes with the ^{1}H NMR spectral events observed in solution for *N*-*p*-methoxybenzylsuccinimides **11xd**, **11yd**, and **11zd** shown in Figure 1. As clearly revealed by the side-view drawings of the dimeric structures shown in Figure 4, the heteroaryl rings are face-to-face juxtaposed to reciprocally exert anisotropic shielding effects on the aryl ring (H_e, H_f, and H_g) and dimethyl protons (in **11yd**) that are positioned on top of the aromatic ring. On the other hand, the oxa-bridgehead methine protons (H_a) are located in-plane with the internal sandwiched aromatic ring and thus are deshielded to show upfield shifts.[27]

Next we describe the additional noncovalent interactions that control the packing of dimeric entities into two- and three-dimensional structures in the crystal. Examination of the crystal packing revealed that the dimeric entities of **11yd**, **11zb**, and **11zd** are mainly driven by π–π stacking interaction to form two-dimensional arrays of dimeric aggregate (Fig. 5). The π–π mean plan separation distances between dimers are 3.49 Å, 3.45 Å, and 3.56 Å, respectively (Table 2). This interdimeric π–π stacking interaction is absent in the association of dimeric entities of **11xa**. As shown in Figure 5a, the external dimethylquinoxaline walls of one dimeric **11yd** pack against the identical walls of the neighbors in an antiparallel manner, like the type **I** depicted in Figure 2. In this packing motif, the methyl groups are concomitantly close to the nitrogen atoms of quinoxaline ring ($d_{N\cdots H}$=2.76/3.06 Å; 2.90/3.17 Å) and the

Table 1
Crystal data and structure refinement for compounds **11xa**, **11zb**, **11yd**, and **11zd**

Identification code	**11xa**	**11zb**	**11yd**	**11zd**
Empirical formula	$C_{44}H_{33}Cl_4N_5O_8$	$(C_{53}H_{39}Cl_4N_5O_9)_2(CHCl_3)$	$(C_{50}H_{45}Cl_4N_5O_9)_2(C_2H_5OH)$	$(C_{54}H_{41}Cl_4\ N_5O_9)_2$
Formula weight	901.55	2182.75	2049.49	2091.44
Crystal size [mm]	0.20×0.13×0.13	0.12×0.06×0.05	0.32×0.31×0.30	0.19×0.11×0.03
Temperature [K]	298	298	298	298
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system, space group	Tetragonal, *I*-42*d*	Triclinic, *P*-1	Triclinic, *P*-1	Triclinic, *P*-1
Unit cell dimensions	*a*=30.8823(17) Å, *b*=30.8823(17) Å, *c*=21.3738(17) Å	*a*=12.7563(19) Å, *b*=15.381(2) Å, *c*=29.160(5) Å, *α*=75.987(3)°, *β*=80.798(3)°, *γ*=73.191(3)°	*a*=11.855(2) Å, *b*=17.704(3) Å, *c*=25.195(4) Å, *α*=83.623(3)°, *β*=76.920(3)°, *γ*=79.775(3)°	*a*=14.784(2) Å, *b*=16.376(3) Å, *c*=23.988(4) Å, *α*=105.364(2)°, *β*=90.004(2)°, *γ*=110.558(2)°
Volume [Å^3]	20,385(2)	5288.9(14)	5055.2(15)	5215.4(15)
Z	16	2	2	2
Density (calcd) [mg/m^3]	1.175	1.371	1.346	1.332
Absorption coefficient [mm^{-1}]	0.282	0.360	10.296	0.288
F(000)	7424	2244	2132	2160
θ range for data collection [°]	1.76–28.36	1.41–25.35	1.17–28.43	1.38–25.68
Index ranges	$-37\leqq h\leqq 39$, $-41\leqq k\leqq 29$, $-19\leqq l\leqq 28$	$-15\leqq h\leqq 15$, $-18\leqq k\leqq 18$, $-35\leqq l\leqq 35$	$-15\leqq h\leqq 15$, $-23\leqq k\leqq 23$, $-33\leqq l\leqq 33$	$-18\leqq h\leqq 18$, $-19\leqq k\leqq 19$, $-29\leqq l\leqq 29$
Reflections collected	64,717	52,926	59,070	52,193
Independent reflections	12,385 [R_{int}=0.0923]	19,338 [R_{int}=0.1730]	23,753 [R_{int}=0.0909]	19,710 [R_{int}=0.0946]
Completeness to *θ*=25.35	98.5%	99.7%	93.4%	99.5%
Max. and min. transmission	0.9650 and 0.9454	0.9839 and 0.9596	0.9176 and 0.9124	0.9909 and 0.9469
Data/restraints/parameters	12,385/0/555	19,338/0/1325	23,753/0/1273	19,710/0/1308
Goodness-of-fit on F^2	1.051	0.782	0.947	0.941
Final *R* indices [$I>2\sigma(I)$]	R_1=0.0919, wR_2=0.2290	R_1=0.0852, wR_2=0.1749	R_1=0.0905, wR_2=0.1996	R_1=0.0976, wR_2=0.2275
R indices (all data)	R_1=0.1526, wR_2=0.2635	R_1=0.2966, wR_2=0.2382	R_1=0.2188, wR_2=0.2410	R_1=0.2267, wR_2=0.2722
$\Delta\rho_{max}$, $\Delta\rho_{min}$ [e Å^{-3}]	0.944, −0.504	0.500, −0.324	0.617, −0.356	1.085, −0.514

$R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$.
$wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma[w(F_o^2)^2]]^{1/2}$.

oxygen atom of methoxy group at the acetal carbon atom ($d_{O\cdots H}$= 2.63/2.76 Å), suggestive of benefit from CH···X (X=N, O) close contacts.[26] Differently from that of **11yd**, the interdimeric packing motifs of **11zb** and **11zd** assume a V-shaped arrangement like the type **J** depicted in Figure 2, as, respectively, shown in Figure 5b and c. In addition to the π–π stacking interaction as the major driving force for dimeric aggregation of **11zb** and **11zd**, the association of dimeric structures is further reinforced by packing motif based on $OCH_3\cdots OCH_3$ interactions[26] using the polarized C–H bonds of methoxy groups of intercalators ($d_{O\cdots H}$: **11zb** 2.51/2.62 Å; **11zd**

Table 2
Selected parameters of the X-ray crystal structures of **11xa**, **11yd**, **11zb**, and **11zd**

	11xa	**11yd**	**11zb**	**11zd**
Monomer[a]				
d_{NN} (Å)	8.41	7.74/7.72	7.89/7.91	7.70/7.65
d_{CC} (Å)	9.49	7.45/7.43	8.00 /8.39	7.48/7.13
$OCH_3\cdots C_{Ph}$ (Å)	—	3.02/3.11	—	3.01/3.49
C_{Ar}–C_{Ar}–*N*–$C_{C=O}$ (°)	72.9	—	51.9/66.5	—
Intradimeric interactions				
Molecular clipping angle (°)	45	81	85	75
π–π mean plan separation (Å)	3.68; 5.05	3.56; 3.82	3.95; 4.06	3.50; 3.70
O–H···N_{Ar} hydrogen bond				
H···N···H distances (Å) [angle (°)]	2.65; 2.82 [64.2]	2.87;3.24 [71.5], 3.19; 3.36 [62.6]	2.75; 2.81 [62.3], 3.15; 3.68 [56.7]	2.77; 3.05 [58.2], 3.09; 3.13 [64.3]
$OCH_3\cdots N_{Ar}$ contact (Å)	—	2.71; 3.36	3.25	2.90; 2.94
Interdimeric interactions				
π–π mean plan separation (Å)	—	3.49	3.45	3.56
$CH_3\cdots N_{Ar}$ (Å)	—	2.76/3.06; 2.90/3.17	—	—
$CH_3\cdots OCH_3$ (Å)	—	2.63;2.76	—	—
$OCH_3\cdots OCH_3$ (Å)	2.83	—	2.51/2.62	2.63; 2.73/2.77
$OCH_3\cdots N_{Ar}$ (Å)	2.64	—	3.05	2.82
$OCH_3\cdots O{=}C$–N (Å)	—	2.78	2.75; 3.08	2.57/3.30
$CH_3\cdots O{=}C$–N (Å)	—	2.73/2.82, 2.84/2.86	—	—
Solvate	—	EtOH[b]	$CHCl_3$[c]	—

[a] Except **11xa**, two conformations were noted for the crystal structure of **11yd**, **11zb**, and **11zd**.
[b] EtOH is distorted.
[c] $d(Cl_3CH\cdots N)$=2.39 Å.

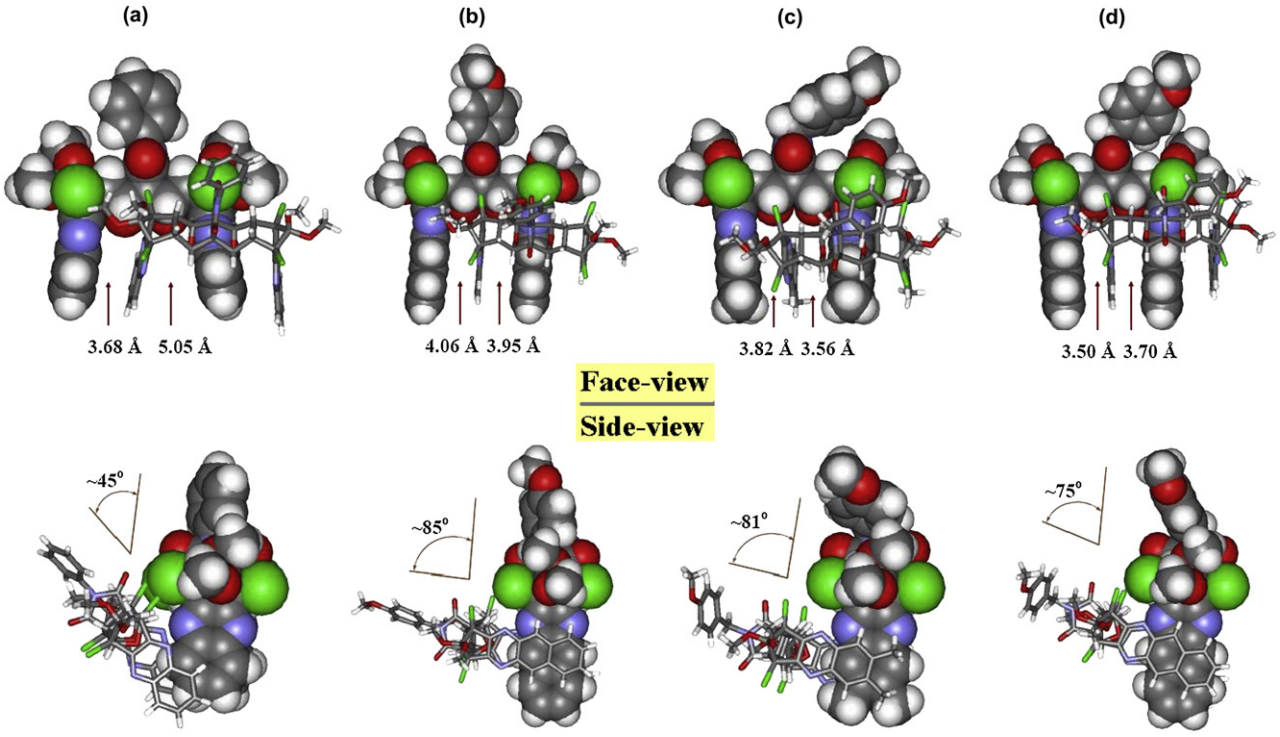


Figure 4. The packing motifs observed for the dimer in crystal using space-filling and stick representations: (a) **11xa**, (b) **11zb**, (c) **11yd**, and (d) **11zd**. Color coding: C, gray; H, white; N, blue; O, red; Cl, green.

2.63/2.73/2.77 Å, Table 2). Additionally, the $OCH_3\cdots N_{Ar}$ close contact between the nitrogen atom in benzoquinoxaline ring and hydrogen atom at the nearby methoxy group of intercalator is also manifestly supportive ($d_{N\cdots H}$: **11zb** 3.05 Å; **11zd** 2.82 Å).

Without π–π stacking interaction between dimers, *N*-phenylsuccinimide **11xa** makes use of the appended *N*-phenyl ring to knit dimeric structures, via CH–π interactions (indicated by Ph–H···N close contact), into a circular molecular column consisted of four arrays of dimeric aggregate as illustrated in Figure 6a. Each of the four dimeric structures is concurrently one of the building blocks of the neighboring circular molecular column, resulting in the formation of interlaced molecular columns. It is interesting to note that the *N*-phenyl and quinoxaline rings involving in the PhH···N close contacts assemble into a four-component configuration (Fig. 6b), in which each *N*-phenyl group binds one quinoxaline ring by the 'edge-to-face' geometry[28] with a distance of 4.35 Å between the centroids and a shortest interatomic distance of $d_{N\cdots H}$=3.26 Å (*m*-CH···N). Each *N*-phenyl group further connects to another quinoxaline ring of neighboring dimer by similar arrangement, but larger spaced out, with centroid-to-centroid distance of 6.50 Å and a shortest interatomic distance of $d_{N\cdots H}$=3.13 Å (*p*-C–H···N). The *N*-phenyl groups themselves also adopt the 'edge-to-face' geometry[28] with a distance of 6.24 Å between the π-ring centroids and a shortest *p*-C–H···*p*-C a distance of 2.99 Å. The circular molecular column is additionally stabilized by interdimeric packing motifs based on $OCH_3\cdots OCH_3$ and $OCH_3\cdots N_{Ar}$ interactions[26] using the polarized C–H bonds of methoxy groups ($d_{O\cdots H}$=2.83 Å, $d_{N\cdots H}$= 2.64 Å, Table 2) as shown in Figure 6a.

Figure 7a shows part of the crystal packing of V-shaped dimers of *N*-*p*-methoxyphenyl succinimide **11zb** displayed on the *ac*-plane that composed of four dimeric units reiterating along the crystallographic *b*-axis to form four molecular arrays, in which molecules of solvating $CHCl_3$ are grasped in position to fill the voids by hydrogen bonding to the nitrogen atom of benzoquinoxaline ring ($Cl_3CH\cdots N$, $d_{N\cdots H}$= 2.39 Å).[26] In this quadruplet arrangement, the two V-shaped molecular arrays, which are aligned in different direction ('head-to-tail'), are held together by the $OC–H_3\cdots O{=}C–N$ interactions between polarized C–H bond of OCH_3 group and electron-enriched carbonyl oxygen of succinimide group ($d_{N\cdots H}$=2.75/3.08 Å, Fig. 7a, Table 2).[10e,26] To unit V-shaped dimeric **11zb** to form the two-dimensional sheet like the quadruplet shown in Figure 7a, the *N*-*p*-methoxyphenyl rings are used as shown in Figure 7b. The *anti*-periplanar display of *p*-methoxyphenyl rings (parallel-displaced geometry),[18,24] which are spaced out by an intercentroid distance of 6.10 Å with shortest interatomic distance of 4.43 Å between *meta*-carbon atoms, are evidently resulted from π–π stacking interactions. Each of the *p*-methoxyphenyl ring then employs its oxygen atoms in CH_3O and O=C–N groups to grip neighboring benzoquinoxaline rings through $H_3C–O\cdots H–C_{Ar}$ and $N–C{=}O\cdots H–C_{Ar}$ close contacts ($d_{O\cdots H}$=2.59/ 2.65 Å, Fig. 7b).[10f,26] The alliance is further stabilized by the packing motif based on the interactions between the polarized C–H bonds of OCH_3 in *p*-methoxyphenyl ring and the nitrogen atom in benzoquinoxaline ring ($d_{N\cdots H}$=2.86 Å).[26]

Although carrying different *N*-substituents in succinimide moiety, the crystal packing of *N*-*p*-methoxybenzyl **11yd** is very similar to that of *N*-*p*-methoxyphenyl **11zb**. The quadruplet shown in Figure 8a discloses that **11yd** chiefly employs electron-enriched carbonyl oxygen of succinimide moiety to stitch together the V-shaped molecular arrays of dimers by means of close contacts with aromatic *ortho*-hydrogen and polarized C–H bond of OCH_3 group at linker ($ArCH_3\cdots O{=}C–N$, $d_{O\cdots H}$=2.73/2.82 and 2.84/2.86 Å; $OC–H_3\cdots O{=}C–N$, $d_{O\cdots H}$=2.78 Å, Table 2). The carbonyl oxygen of succinimide moiety further contacts closely with the *ortho*-hydrogen atom of appended *N*-*p*-methoxybenzyl group to apply $ArH\cdots O{=}C–N$ interaction ($d_{O\cdots H}$=2.56 Å), which works together with the $ArH\cdots N_{Ar}$ contact ($d_{N\cdots H}$=2.95, Fig. 8a Å), grasps the neighboring *p*-disubstituted benzene rings to line up in parallel-displaced geometry[18,24] as shown in Figure 8b. An intercentroid distance of 5.19 Å with shortest interatomic distance of 5.18 Å between *meta*- and CH_2-attached carbon atoms evidently benefits the π–π stacking interaction, and thus stabilize the interdimeric packing of **11yd** dimers.

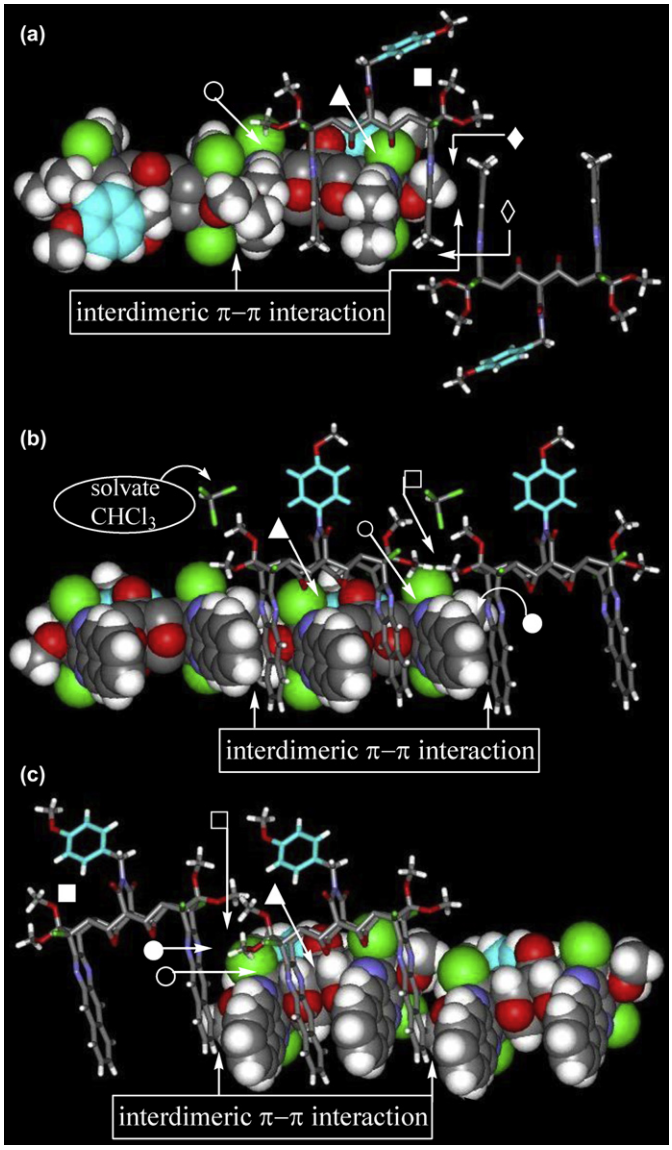


Figure 5. Intradimeric and interdimeric packing motifs observed for the dimer in crystal using space-filling and stick representations: (a) **11yd** along the *c*-axis, (b) **11zb** along the *b*-axis, and (c) **11zd** along the *a*-axis. Packing-motif icon: ■, $OCH_3\cdots C_{Ph}$ contact; ○, intradimeric $OCH_3\cdots N_{Ar}$ contact; •, interdimeric $OCH_3\cdots N_{Ar}$ contact; ▲, $OH\cdots N_{Ar}$ hydrogen bond; ◆, $CH_3\cdots N_{Ar}$ contact; ◇, $CH_3\cdots OCH_3$ contact; □, $OCH_3\cdots OCH_3$ contact. For clarity, the distorted solvate EtOH in **11yd** and some hydrogen atoms are omitted. Color coding: C, gray; H, white; N, blue; O, red; Cl, green; benzene ring, cyan.

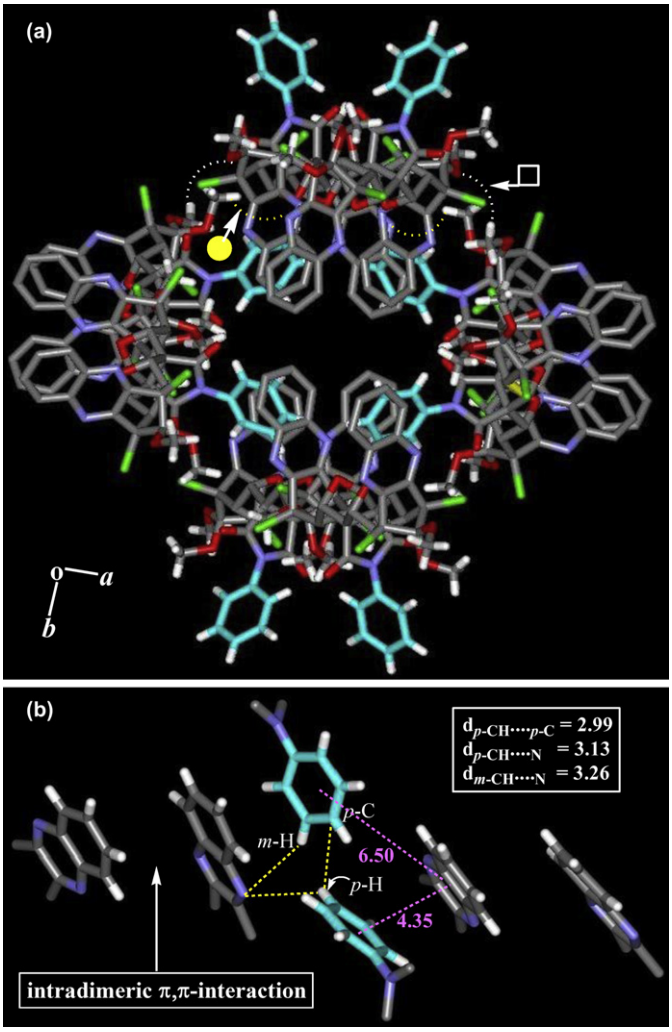


Figure 6. The packing motifs observed for crystal **11xa**. (a) Showing a circular molecular column formed by dimeric structures viewed along the *c*-axis on the *ab*-plane and the $OCH3\cdots NAr$ (•) and$OCH_3\cdots OCH_3$ (□) close contacts between dimeric structures. (b) Illustrating the center-to-center distances between *N*-phenyl (cyan colored) and quinoxaline rings and their roles in the interdimeric connection by *m*-CH···N and *p*-C–H···N interactions. The *N*-phenyl groups adopt the 'edge-to-face' geometry with a distance of 6.24 Å between the π-ring centroids and a shortest *p*-C–H···*p*-C a distance of 2.99 Å. Distances are in Å unit. For clarity, the irrelevant hydrogen atoms are omitted.

An examination of the crystal packing of **11zd** reveals that the appended *N*-*p*-methoxybenzyl group plays a major role of uniting V-shaped dimers of **11zd**. The noteworthy feature is that the paired dimers reciprocally insert one of their two *N*-*p*-methoxybenzyl groups into each other, such that the methoxy hydrogen and imide oxygen atoms are in close contact to fasten the paired dimers through $Ar\text{–}OCH_3\cdots O{=}C\text{–}N$ interactions ($d_{O\cdots H}$=2.57/3.31 Å, Fig. 9a). As shown in Figure 9b, these two 'internal' *N*-*p*-methoxybenzyl groups are *anti*-periplanar aligned and displaced by an intercentroid distance of 7.04 Å with shortest interatomic distance of 4.13 Å between *ortho* carbon and hydrogen atoms. This geometrical alignment is secured by $Ar\text{–}H\cdots O{=}C\text{–}N$ contact ($d_{O\cdots H}$= 2.60 Å). Within the paired dimeric structures, the phenyl rings of internal and external *N*-*p*-methoxybenzyl groups adopt face-titled-T structure[18,28a] with dihedral angle of about 60° and shortest C–C distance of 4.34 Å, appropriate for CH–π interaction ($d_{p\text{-}C\cdots m\text{-}H}$= 3.57 Å)[28] and $ArH\cdots OCH_3$ contacts ($d_{O\cdots H}$=3.16 Å). The external *N*-*p*-methoxybenzyl groups of adjacent paired dimers, which are *anti*-periplanar aligned and far apart, employ $Ar\text{–}OCH_3\cdots O{=}C\text{–}N$ contacts to connect the nearby paired dimers ($d_{O\cdots H}$=3.30 Å, Fig. 9a).

3. Conclusion

In summary, 12 [7,7]orthocyclophanes (Scheme 3) comprising two sidewalls (phane parts) made of quinoxaline, dimethylquinoxaline, or benzoquinoxaline rings and a septuple-bridged linker incorporated with succinimide moiety that carries phenyl, *p*-methoxyphenyl, *p*-hydroxyphenyl, or *p*-methoxybenzyl appendants were synthesized via a three-step synthetic route (Scheme 1). The tendency of these U-shaped [7,7]orthocyclophanes to self-assemble and form reciprocally clipped V-shaped dimeric entities has been studied and supported by concentration-variant ^{1}H NMR spectroscopy and X-ray crystal structural analysis. Examination of the crystal packing revealed that the π–π stacking interaction is the key driving force for self-assembly to form dimeric entity and

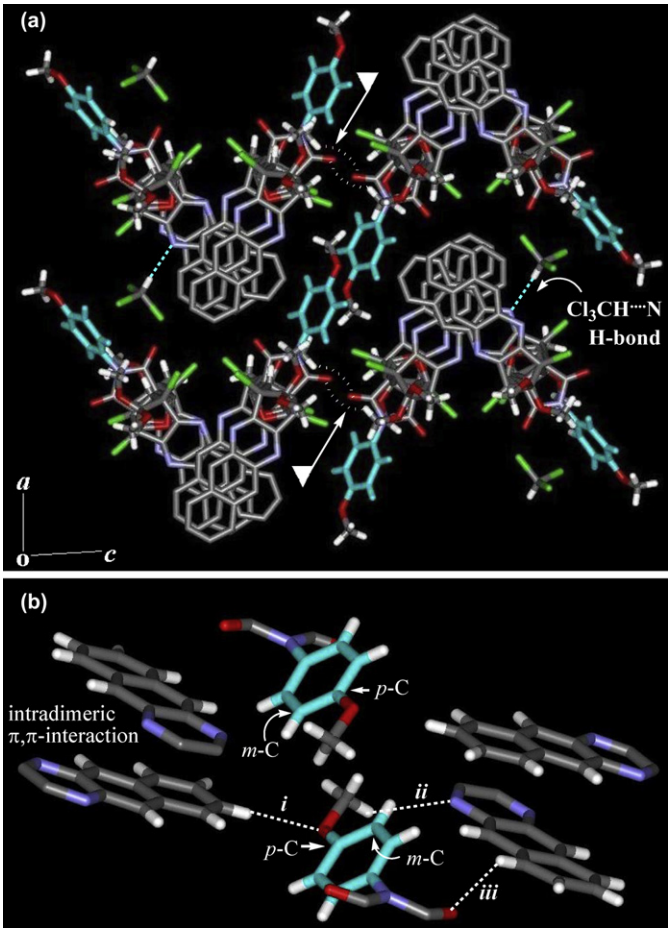


Figure 7. The packing motifs observed for crystal **11zb**. (a) Viewed along the *b*-axis showing the assembly of four V-shaped molecular arrays of dimeric **11zb**, the $OCH_3\cdots O{=}C{-}N$ (▼) close contacts, and the interaction of solvating $CHCl_3$ with benzoquinoxaline ring ($d_{N\cdots H}$=2.39 Å). (b) Illustrating the parallel-displaced geometry of *N*-methoxyphenyl rings (cyan colored) and their role in uniting V-shaped dimeric **11zb** by (*i*) $H_3C{-}O\cdots H{-}C_{Ar}$ (2.59 Å), (*ii*) $OCH_3\cdots N_{Ar}$ (2.86 Å), and (*iii*) $N{-}C{=}O\cdots H{-}C_{Ar}$ (2.65 Å) close contacts.

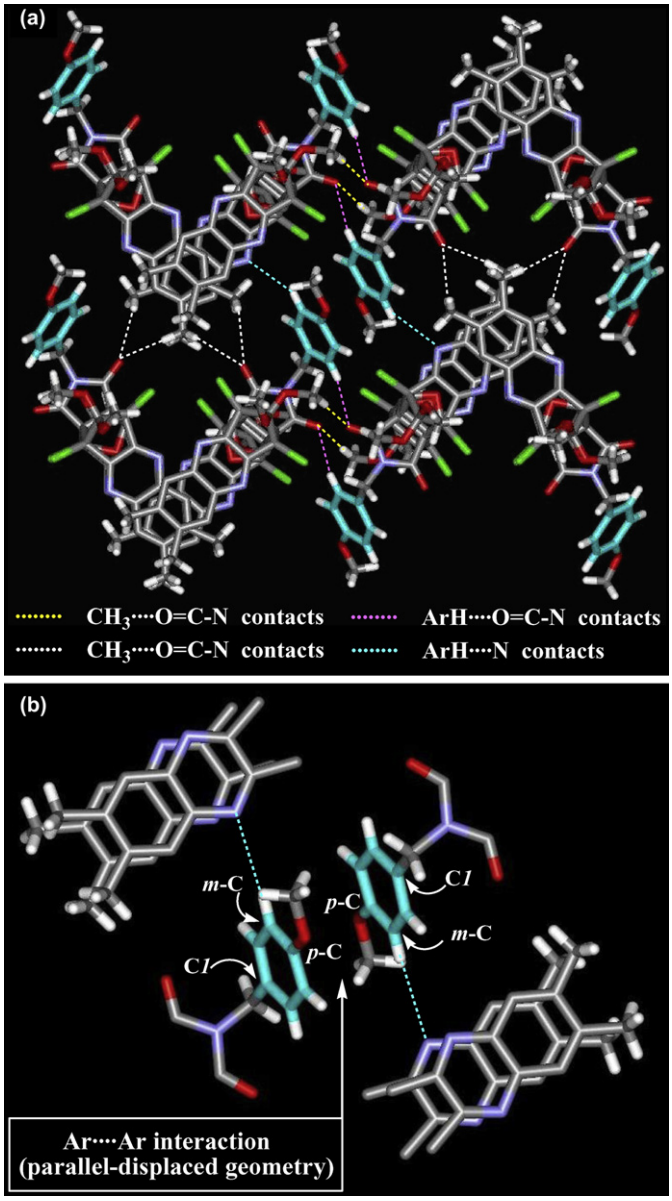


Figure 8. The packing motifs observed for crystal **11yd**. (a) Showing the knitting of V-shaped molecular arrays of dimeric **11yd** by four kinds of close contacts. (b) Illustrating the parallel-displaced geometry of *N*-*p*-methoxybenzylic rings with intercentroid distance of 5.19 Å and shortest interplanar distance of 5.18 Å (C1–*m*-C). For clarity, the irrelevant hydrogen atoms are omitted.

two-dimensional arrays of dimeric aggregate. Additional noncovalent interactions involving nitrogen atom in hetroaromatic ring, the polar groups (OCH_3 and N–C=O) of intercalator, and particularly the *N*-appended aryl ring, which are attributed cooperatively to the formation of three-dimensional crystalline architectures in the crystals, were also disclosed. In combination, these results suggest that design and synthesis of quinoxaline-based multi-bridged orthocyclophanes that have potential of building up complex crystalline architectures via self-assembly and cross-assembly with guest molecules could be realized by synthetic strategy shown in Scheme 1.

4. Experimental

4.1. General experimental

Melting points were determined in capillaries on a Büchi Melting Point B-540 apparatus, and were uncorrected. Infrared (IR) spectra were recorded on a JASCO FT/IR-460 spectrophotometer as a solid suspended in a KBr disk. ^1H and ^{13}C NMR spectra were collected on a Bruker DPX-400 or Varian-Unity INOVA-500 spectrometer using $CDCl_3$ as solvent (unless otherwise specified). Coupling constants are reported in hertz. The number of attached hydrogen on the carbon atom was determined by the DEPT analysis and is denoted as s (C), d (CH), t (CH_2), and q (CH_3). The assignment of proton and carbon NMR peaks for some compounds was supported by $^1H{-}^1H$ COSY and HMQC spectra. Mass (MS) spectra were obtained on a Finnigan/Thermo Quest MAT 95XL instrument by the FAB mode with 3-nitrobenzyl alcohol (3-NBA) as the matrix. Ultraviolet/visible (UV/vis) absorption spectra were measured with HP 8453 UV–Visible Photodiode Array spectrophotometer. Fluorescence emission spectra were obtained using a Varian Cary-Eclipse fluorescence spectrometer. Spectrometric grade solvent and quartz cell (1×1 cm^2) were used. The X-ray crystallographic data were recorded with a Bruker AXS SMART APEX CCD X-ray diffractometer. Graphite monochromatized Mo Kα 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). Analytical thin-layer chromatography (TLC) was performed on E. Merck silica gel 60 F_{254} plate (0.20 mm). Flash chromatography

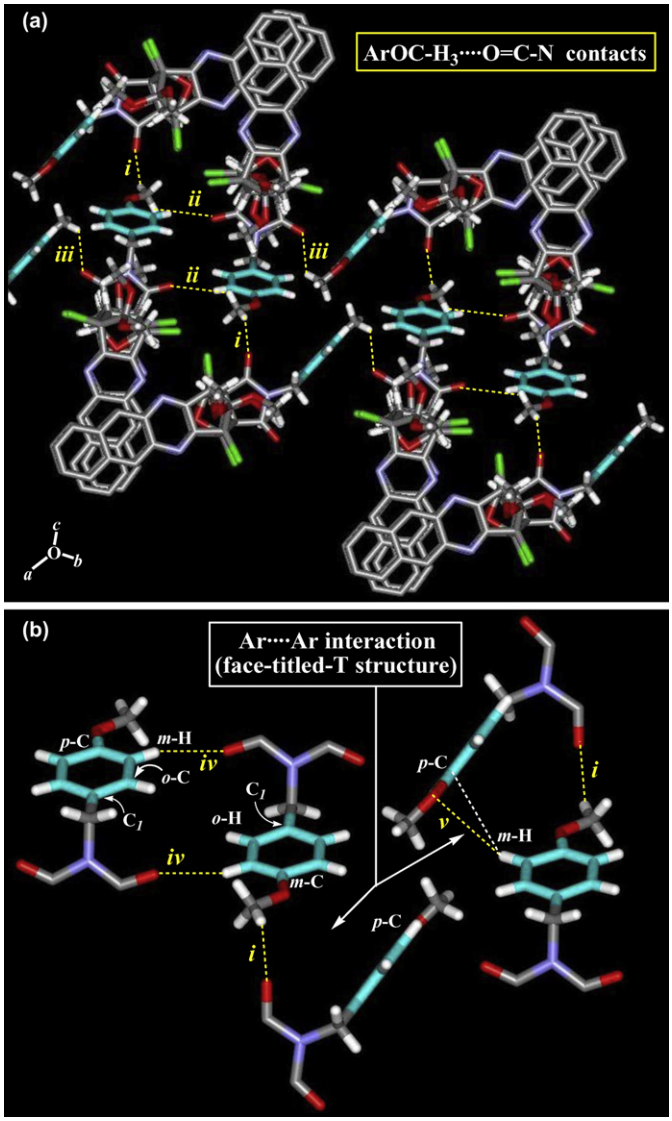


Figure 9. The packing motifs observed for crystal **11zd**. (a) Showing the connection of V-shaped molecular arrays of dimeric **11zd** by $ArOCH_3\cdots O{=}C{-}N$ contacts with $d_{H\cdots O}$=*i*: 2.57 Å, *ii*: 3.31 Å, *iii*: 3.30 Å; (b) showing two *anti*-periplanar aligned *N*-*p*-methoxybenzyl groups that are displaced by an intercentroid distance of 7.04 Å with shortest interatomic distance of 4.13 Å between *o*-C and *o*-H atoms and held by $ArH\cdots O{=}C{-}N$ contacts (*iv*: $d_{H\cdots O}$=2.60 Å), and two paired *N*-*p*-methoxybenzyl groups that are face-titled-T structured by a dihedral angle of about 60° with shortest *m*-C–*p*-C distance of 4.34 Å ($d_{p\text{-}C\cdots m\text{-}H}$=3.57 Å) and $ArH\cdots OCH_3$ contacts (*v*: $d_{O\cdots H}$=3.16 Å). Hydrogen atoms at the intercalators and aromatic rings except *N*-methoxybenzyl rings are omitted for clarity.

was performed on E. Merck silica gel (230–400 mesh). All solvents used were either reagent grade or were distilled prior to use.

4.2. Syntheses

*4.2.1. 5,6,7,8,14,15,16,17-Octachloro-21,21,22,22-tetramethoxy-19,20-dioxaoctacyclo[10.6.1.1^{3,10}.1^{5,8}.1^{14,17}.0^{2,11}.0^{4,9}.0^{13,18}]docosa-6,15-dien-2,11-dicarboxylic anhydride (**5o**).* A mixture of dioxatetracyclic bis-alkene anhydride **4**[17] (0.20 g, 0.86 mmol) and 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadine (**1**, 0.50 g, 1.89 mmol) was heated with stirring at 90 °C for 2 h. After cooling, the resultant white solid was filtered, collected, rinsed with ether, and dried to give *syn*-bis-DA-adduct **5o** (0.43 g, 65%) as a white solid, which was pure enough and was used without purification for the next step: mp 348–349 °C (decomp.); IR (KBr, cm^{-1}) 1786 (s), 1192 (s), 922 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.88 (s, 4H), 3.56 (s, 6H), 3.50 (s, 6H), 2.90 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1 (s), 127.3 (s), 112.8 (s), 80.2 (d), 75.1 (s), 74.8 (s), 53.5 (d), 52.8 (q), 51.9 (q); MS (FAB$^+$) *m*/*z* (%) 760 (M$^+$+4, 9), 758 (M$^+$+2, 6), 756 (M$^+$, 3), 728 (15), 726 (25), 724 (27); HRMS (FAB$^+$) Calcd for $C_{26}H_{21}Cl_8O_9$ (M$^+$+H): 756.8688. Found: 756.8705; Anal. Calcd for $C_{26}H_{20}Cl_8O_9$: C, 41.09; H, 2.65; O, 18.95. Found: C, 41.53; H, 2.94; O, 18.65.

*4.2.2. Preparation of N-substituted succinimides **9a–d**.* The *N*-sub-understituted succinimides **9a–d** were prepared in two steps by following essentially the reported procedure.[17] The dioxatetracyclic bis-alkene anhydride **4** was subjected to the reaction with aniline (**7a**), 4-methoxybenzenamine (**7b**), 4-aminophenol (**7c**), or *p*-methoxybenzylamine (**7d**) in THF promoted by *n*-BuLi at −78 °C to rt, and the resultant amic acid **8**, without isolation, was treated with sodium acetate in acetic anhydride and stirred at 60 °C for 2 days to provide *N*-substituted succinimides **9a**, **9b**, **9c**, and **9d**[17] in 40%, 48%, 40%, and 44% overall yield, respectively.

*4.2.2.1. N-Phenyl-11,12-dioxatetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-dien-2,7-carboximide (**9a**).* Mp 264 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.43 (m, 3H), 7.01–7.03 (m, 2H), 6.77 (s, 4H), 5.36 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2 (s), 139.2 (d), 131.1 (s), 129.2 (d), 129.0 (d), 126.0 (d), 81.6 (d), 69.1 (s); MS (FAB$^+$) *m*/*z* (%) 307 (M$^+$, 31), 289 (27), 281 (20), 136 (98), 109 (82), 95 (97), 73 (58), 69 (100); HRMS (FAB$^+$) Calcd for $C_{18}H_{13}NO_4$ (M$^+$): 307.0845. Found: 307.0847.

*4.2.2.2. N-(4-Methoxyphenyl)-11,12-dioxatetracyclo[6.2.1.1^{3,6}.0^{2,7}]-dodeca-4,9-dien-2,7-carboximide (**9b**).* Mp 284–285 °C (acetone); IR (KBr, cm^{-1}) 1717 (s), 1607 (w), 1513 (m), 1185 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92 (s, 4H), 6.75 (s, 4H), 5.35 (s, 4H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5 (s), 159.8 (s), 139.2 (d), 127.3 (d), 123.7 (d), 114.5 (d), 81.6 (d), 69.0 (s), 55.5 (q); MS (FAB$^+$) *m*/*z* (%) 337 (M$^+$, 20), 307 (28), 289 (31), 263 (20), 237 (22); HRMS (FAB$^+$) Calcd for $C_{19}H_{15}NO_5$ (M$^+$): 337.0950. Found: 337.0956; Anal. Calcd for $C_{19}H_{15}NO_5$: C, 67.65; H, 4.48; N, 4.15; O, 23.72. Found: C, 67.33; H, 4.33; N, 4.11; O, 23.68.

*4.2.2.3. N-(4-Acetoxyphenyl)-11,12-dioxatetracyclo[6.2.1.1^{3,6}.0^{2,7}]-dodeca-4,9-dien-2,7-carboximide (**9c**).* Mp 259–260 °C (acetone); IR (KBr, cm^{-1}) 1708 (s), 1512 (m), 1210 (s), 1126 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, 2H, *J*=8.8 Hz), 7.05 (d, 2H, *J*=8.8 Hz), 6.75 (s, 4H), 5.35 (s, 4H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0 (s), 168.9 (s), 150. 5 (s), 139.2 (d), 128.4 (s),127.0 (d), 122.4 (d), 81.6 (d), 69.1 (s), 21.1 (q); MS (FAB$^+$) *m*/*z* (%) 366 (M$^+$+H, 16), 339 (12), 307 (85), 289 (64), 137 (100), 77 (95); HRMS (FAB$^+$) Calcd for $C_{20}H_{16}NO_6$ (M$^+$+H): 366.0972. Found: 366.0985; Anal. Calcd for $C_{20}H_{15}NO_6$: C, 65.75; H, 4.14; N, 3.83; O, 26.28. Found: C, 65.39; H, 3.72; N, 4.42; O, 26.12.

*4.2.3. Diels–Alder reactions of TDCp and N-substituted succinimides **9a–d**. Preparation of syn-bis-DA-adducts **5a–d**.* A mixture of *N*-substituted succinimide **9a**, **9b**, **9c**, or **9d** (1 mmol) and TDCp (**1**, 2.2 mmol) without solvent or in toluene was heated with stirring at reflux temperature for 2 days. After cooling solvent was removed at vacuum and the resultant white solid was filtered, washed with small amount of ether, and dried to give *syn*-bis-DA-adduct **5a** (90%), **5b** (90%), **5c** (92%), or **5d** (96%) as white solid, pure enough for the next step.

*4.2.3.1. N-Phenyl-5,6,7,8,14,15,16,17-octachloro-21,21,22,22-tetramethoxy-19,20-dioxaoctacyclo[10.6.1.1^{3,10}.1^{5,8}.1^{14,17}.0^{2,11}.0^{4,9}.0^{13,18}]docosa-6,15-dien-2,11-dicarboximide (**5a**).* Mp 315–316 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.59 (m, 3H), 7.19–7.20 (m, 2H), 4.91 (s, 4H), 3.56 (s, 6H), 3.49 (s, 6H), 2.92 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7 (s), 130.7 (s), 130.0 (s), 129.9 (d), 127.2 (d), 126.4 (d), 112.9 (s), 79.9 (d), 75.2 (s), 72.1 (s), 53.8 (d), 52.8 (q), 51.7 (q); MS

(FAB$^+$) *m*/*z* (%) 838 (24), 836 (33), 834 (26), 802 (18), 800 (26), 798 (25), 460 (25), 307 (100), 289 (97), 71 (86); HRMS (FAB$^+$) Calcd for $C_{32}H_{26}Cl_8NO_8$ (M^++H): 831.9161. Found: 831.9175.

*4.2.3.2. N-(4-Methoxyphenyl)-5,6,7,8,14,15,16,17-octachloro-21,21,22,22-tetramethoxy-19,20-dioxaoctacyclo[10.6.1.1^{3,10}.1^{5,8}.1^{14,17}.0^{2,11}.0^{4,9}.0^{13,18}]docosa-6,15-dien-2,11-dicarboximide (**5b**).* Mp 348–349 °C ($CHCl_3$/hexane); IR (KBr, cm^{-1}) 1718 (s), 1512 (m), 1185 (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (d, 2H, *J*=9.1 Hz), 7.06 (d, 2H, *J*=9.1 Hz), 4.91 (s, 4H), 3.87 (s, 3H), 3.58 (s, 6H), 3.52 (s, 6H), 2.92 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7 (s), 160.2 (s), 127.3 (d), 126.9 (s), 122.9 (s), 114.9 (d), 112.6 (s), 79.6 (d), 74.9 (s), 71.7 (s), 55.3 (q), 53.5 (d), 52.5 (q), 51.4 (q); MS (FAB$^+$) *m*/*z* (%) 866 (M^++H+4, 7), 864 (M^++H+2, 6), 862 (M^++H, 2), 830 (10), 828 (9), 307 (20), 253 (22), 136 (74); HRMS (FAB$^+$) Calcd for $C_{33}H_{28}Cl_8NO_9$ (M^++H): 861.9267. Found: 861.9280; Anal. Calcd for $C_{33}H_{27}Cl_8NO_9$: C, 45.81; H, 3.15; N, 1.62; O, 16.45. Found: C, 45.87; H, 3.08; N, 2.01; O, 16.64.

4.2.3.3. N-(4-Acetoxyphenyl)-5,6,7,8,14,15,16,17-octachloro-21,21,22,22-tetramethoxy-19,20-dioxaoctacyclo[10.6.1.1^{3,10}.1^{5,8}.1^{14,17}.0^{2,11}.0^{4,9}.0^{13,18}]docosa-6,15-dien-2,11-dicarboximide (5c). Mp 354–355 °C ($CHCl_3$/hexane); IR (KBr, cm^{-1}) 1717 (s), 1608 (w), 1505 (m), 1368 (m), 1212 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, 2H, *J*=8.8 Hz), 7.23 (d, 2H, *J*=8.8 Hz), 4.92 (s, 4H), 3.56 (s, 6H), 3.50 (s, 6H), 2.34 (s, 3H), 2.90 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6 (s), 168.8 (s), 151.5 (s), 128.0 (s), 127.4 (s), 127.2 (d), 123.1 (d), 112.9 (s), 79.9 (d), 75.2 (s), 72.1 (s), 53.8 (q), 52.8 (d), 51.7 (q), 21.0 (q); MS (FAB$^+$) *m*/*z* (%) 892 (M^++H+2, 15), 890 (M^++H, 17), 858 (27), 856 (30), 854 (15), 664 (28), 307 (80), 253 (72); HRMS (FAB$^+$) Calcd for $C_{34}H_{28}Cl_8NO_{10}$ (M^++H): 889.9216. Found: 889.9227; Anal. Calcd for $C_{34}H_{27}Cl_8NO_{10}$: C, 45.72; H, 3.05; N, 1.57; O, 17.91. Found: C, 45.60; H, 3.04; N, 1.74; O, 17.51.

*4.2.3.4. N-(4-Methoxybenzyl)-5,6,7,8,14,15,16,17-octachloro-21,21,22,22-tetramethoxy-19,20-dioxaoctacyclo[10.6.1.1^{3,10}.1^{5,8}.1^{14,17}.0^{2,11}.0^{4,9}.0^{13,18}]docosa-6,15-dien-2,11-dicarboximide (**5d**).* Mp 299–301 °C; IR (KBr, cm^{-1}) 1708 (s), 1188 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J*=8.6 Hz, 2H), 6.92 (d, *J*=8.6 Hz, 2H), 4.79 (s, 4H), 4.59 (s, 2H), 3.81 (s, 3H), 3.43 (s, 6H), 3.25 (s, 6H), 2.54 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2 (s), 159.6 (s), 130.8 (d), 127.2 (s), 126.8 (s), 114.5 (d), 112.7 (s), 79.8 (d), 75.2 (s), 71.9 (s), 55.3 (q), 53.3 (d), 52.6 (q), 51.4 (q), 42.4 (t); MS (FAB$^+$) *m*/*z* (%) 880 (M^++6, 14), 878 (M^++4, 14), 876 (M^++2, 8), 846 (22), 844 (27), 842 (27), 257 (33), 255 (58), 253 (63), 207 (30), 135 (99), 121 (100); HRMS (FAB$^+$) Calcd for $C_{34}H_{30}Cl_8NO_9$ (M^++H): 875.9429; Found: 875.9435; Anal. Calcd for $C_{34}H_{29}Cl_8NO_9$: C, 46.45; H, 3.32; N, 1.59. Found: C, 46.88; H, 3.54; N, 1.35.

4.2.4. General procedure for the preparation of bis-α-ketones. A suspension of $NaIO_4$ (2.50 mmol) and $RuCl_3\cdot 3H_2O$ (0.11 mmol) in water (3 mL) was added in portions to an ice-cooled suspension of *syn*-bis-DA-adduct **5o**, **5a**, **5b**, **5c**, or **5d** (1.0 mmol) in $CHCl_3$ (10 mL) and CH_3CN (10 mL). The resulting dark orange colored mixture was stirred at 0–5 °C for a period of 12–24 h, monitored by TLC and ^{1}H NMR. After completion of reaction, the mixture was then added with water (50 mL) and extracted with CH_2Cl_2 or $CHCl_3$ (2×15 mL). The combined organic phase was washed with water (2×20 mL), dried over $MgSO_4$, filtered by suction through a pad of silica gel to remove any ruthenium derived residue, and evaporated. Purification by recrystallization afforded pale yellow platelets of bis-α-diketone **6**.

*4.2.4.1. 5,8,14,17-Tetrachloro-21,21,22,22-tetramethoxy-6,7,15,16-tetraoxo-19,20-dioxaoctacyclo[10.6.1.1^{3,10}.1^{5,8}.1^{14,17}.0^{2,11}.0^{4,9}.0^{13,18}]docosa-2,11-dicarboxylic anhydride (**6o**).* Reaction time 24 h; Yield 96%; mp>400 °C (decomp.); IR (KBr, cm^{-1}) 1786 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.81 (s, 4H), 3.68 (s, 6H), 3.50 (s, 6H), 3.12 (s, 4H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 186.9 (s), 166.0 (s), 103.3 (s), 82.0 (d), 77.9 (s), 72.3 (s), 55.6 (d), 53.5 (q), 53.4 (q); MS (FAB$^+$) *m*/*z* (%) 685 (M^++H^+4, 40), 683 (M^++H^+2, 46), 681 (M^++H, 24), 597 (33), 595 (61), 593 (50), 229 (48), 187 (82), 149 (100); HRMS (FAB$^+$) Calcd for $C_{26}H_{21}Cl_4O_{13}$ (M^++H): 680.9731. Found: 680.9742; Anal. Calcd for $C_{26}H_{20}Cl_4O_{13}$: C, 45.77; H, 2.95; O, 30.49. Found: C, 46.15; H, 3.38; O, 30.26.

*4.2.4.2. N-Phenyl-5,8,14,17-tetrachloro-21,21,22,22-tetramethoxy-6,7,15,16-tetraoxo-19,20-dioxaoctacyclo[10.6.1.1^{3,10}.1^{5,8}.1^{14,17}.0^{2,11}.0^{4,9}.0^{13,18}]docosa-2,11-dicarboximide (**6a**).* Reaction time 24 h; Yield 85%; mp>400 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.63 (m, 3H), 7.18–7.20 (m, 2H), 4.88 (s, 4H), 3.67 (s, 6H), 3.50 (s, 6H), 3.12 (s, 4H); MS (FAB$^+$) *m*/*z* (%) 758 (M^++H+2, 12), 756 (M^++H, 10), 329 (28), 307 (99), 289 (90), 176 (70), 77 (94); HRMS (FAB$^+$) Calcd for $C_{32}H_{26}Cl_4NO_{12}$ (M^++H): 756.0204. Found: 756.0201; Anal. Calcd for $C_{32}H_{25}Cl_4NO_{12}$: C, 50.75; H, 3.33; N, 1.85; O, 25.35. Found: C, 50.33; H, 3.48; N, 1.68; O, 25.29.

*4.2.4.3. N-(4-Methoxyphenyl)-5,8,14,17-tetrachloro-21,21,22,22-tetramethoxy-6,7,15,16-tetraoxo-19,20-dioxaoctacyclo[10.6.1.1^{3,10}.1^{5,8}.1^{14,17}.0^{2,11}.0^{4,9}.0^{13,18}]docosa-2,11-dicarboximide (**6b**).* Reaction time 12 h; Yield 92%; mp 299 °C (decomp.); IR (KBr, cm^{-1}) 1778 (s), 1720 (s), 1511 (m), 1256 (m), 1195 (m), 1124 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (s, 4H), 4.83 (s, 4H), 3.88 (s, 3H), 3.68 (s, 6H), 3.50 (s, 6H), 3.10 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.2 (s), 170.3 (s), 156.0 (s), 127.2 (d), 122.3 (s), 115.3 (d), 102.0 (s), 80.5 (d), 76.0 (s), 68.4 (s), 55.7 (q), 54.5 (d), 52.9 (q), 52.3 (q); MS (FAB$^+$) *m*/*z* (%) 788 (M^++H+2, 45), 786 (M^++H, 35), 785 (M^+, 11), 752 (15), 370 (27), 289 (28), 136 (98), 77 (82); HRMS (FAB$^+$) Calcd for $C_{33}H_{28}Cl_4NO_{13}$ (M^++H): 786.0309. Found: 786.0309; Anal. Calcd for $C_{33}H_{27}Cl_4NO_{13}$: C, 50.34; H, 3.46; N, 1.78; O, 26.42. Found: C, 49.85; H, 3.61; N, 1.74; O, 26.37.

*4.2.4.4. N-(4-Acetoxyphenyl)-5,8,14,17-tetrachloro-21,21,22,22-tetramethoxy-6,7,15,16-tetraoxo-19,20-dioxaoctacyclo[10.6.1.1^{3,10}.1^{5,8}.1^{14,17}.0^{2,11}.0^{4,9}.0^{13,18}]docosa-2,11-dicarboximide (**6c**).* Reaction time 12 h; Yield 90%; mp 312 °C (decomp.); IR (KBr, cm^{-1}) 1778 (s), 1726 (s), 1507 (w), 1372 (w), 1197 (s), 1125 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, 2H, *J*=8.8 Hz), 7.22 (d, 2H, *J*=8.8 Hz), 4.84 (s, 4H), 3.67 (s, 6H), 3.50 (s, 6H), 3.09 (s, 4H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.2 (s), 169.9 (s), 168.9 (s), 151.5 (s), 127.2 (s), 126.9 (d), 123.4 (d), 102.0 (s), 80.5 (d), 76.0 (s), 68.4 (s), 54.5 (d), 52.8 (q), 52.3 (q), 21.1 (q); MS (FAB$^+$) *m*/*z* (%) 818 (M^++H+4, 50), 816 (M^++H+2, 80), 814 (M^++H, 74), 728 (25), 391 (34), 370 (94), 289 (90), 138 (100), 77 (97); HRMS (FAB$^+$) Calcd for $C_{34}H_{28}Cl_4NO_{14}$ (M^++H): 814.0258. Found: 814.0254; Anal. Calcd for $C_{34}H_{27}Cl_4NO_{14}$: C, 50.08; H, 3.34; N, 1.72; O, 27.47. Found: C, 49.80; H, 3.33; N, 1.68; O, 27.52.

*4.2.4.5. N-(4-Methoxybenzyl)-5,8,14,17-tetrachloro-21,21,22,22-tetramethoxy-6,7,15,16-tetraoxo-19,20-dioxaoctacyclo[10.6.1.1^{3,10}.1^{5,8}.1^{14,17}.0^{2,11}.0^{4,9}.0^{13,18}]docosa-2,11-dicarboximide (**6d**).* Reaction time 12 h; Yield 98%; mp 354–361 °C (decomp.); IR (KBr, cm^{-1}) 1778 (s), 1708 (s), 1199 (s), 667 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J*=8.7 Hz, 2H), 6.95 (d, *J*=8.7 Hz, 2H), 4.69 (s, 4H), 4.62 (s, 2H), 3.82 (s, 3H), 3.44 (s, 6H), 3.43 (s, 6H), 2.68 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.2 (s), 170.4 (s), 159.9 (d), 130.7 (s), 126.2 (s), 114.7 (d), 101.8 (s), 80.5 (d), 76.0 (s), 68.4 (s), 55.3 (q), 54.1 (d), 52.6 (q), 52.1 (q), 42.7 (t); MS (FAB$^+$) *m*/*z* (%) 802 (M^++H+2, 7), 800 (M^++H, 6), 799 (M^+, 6); HRMS (FAB$^+$) Calcd for $C_{34}H_{30}Cl_4NO_{13}$ (M^++H): 800.0466. Found: 800.0480; Anal. Calcd for $C_{34}H_{29}Cl_4NO_{13}$: C, 50.96; H, 3.65; N, 1.75. Found: C, 51.03; H, 3.59; N, 1.76.

*4.2.5. General procedure for the preparation of quinoxaline-based septuple-bridged [7,7]orthocyclophanes **11**.* *o*-Phenylenediamine

(**10x**), 4,5-dimethylbenzene-1,2-diamine (**10y**), or naphthalene-2,3-diamine (**10z**) (1.10 mmol) was added to a solution of bis-α-diketone **6o**, **6a**, **6b**, **6c**, or **6d** (0.50 mmol) in chlorobenzene (12.5 mL) containing a catalytic amount of zinc acetate (0.1 equiv) or trifluoroacetic acid (a few drops) and 0.4 nm molecular sieve (for the case of **10x**). The reaction mixture was heated under reflux for hours, monitored by TLC and ^{1}H NMR. The reaction mixture was filtered to remove salt and the filtrate was concentrated. The residue was purified via recrystallization to afford pure compound **11**.

*4.2.5.1. 7,14,24,31-Tetraaza-5,16,22,33-tetrachloro-37,37,38,38-tetramethoxy-35,36-dioxadodecacyclo[18.14.1.1^{3,18}.1^{5,16}.1^{22,33}.0^{2,19}.0^{4,17}.0^{6,15}.0^{8,13}.0^{21,34}.0^{22,33}.0^{25,30}]octatriaconta-6(15),7,9,11,13,23(33),25,27,29,30-decaene-2,19-dicarboxylic anhydride (**11xo**).* Reaction time 48 h; Yield 60%; mp>400 °C ($CHCl_3$); IR (KBr, cm^{-1}) 1790 (s), 1516 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, J_1=6.3 Hz, J_2=3.5 Hz, 4H), 7.56 (dd, J_1=6.3 Hz, J_2=3.5 Hz, 4H), 4.49 (s, 4H), 3.73 (s, 6H), 3.33 (s, 6H), 3.27 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9 (s), 151.0 (s), 142.3 (s), 129.4 (d), 128.9 (d), 112.3 (s), 79.8 (d), 73.6 (s), 72.0 (s), 53.9 (d), 52.5 (q), 52.3 (q); MS (FAB$^+$) *m*/*z* (%) 830 (M$^+$+6, 57), 829 (M$^+$+4+H, 100), 828 (M$^+$+4, 92), 827 (M$^+$+2+H, 95); HRMS (FAB$^+$) Calcd for $C_{38}H_{29}Cl_4N_4O_9$ (M$^+$+H): 825.0683. Found: 825.0687.

*4.2.5.2. 7,14,24,31-Tetraaza-5,16,22,33-tetrachloro-37,37,38,38-tetramethoxy-10,11,27,28-tetramethyl-35,36-dioxadodecacyclo[18.14.1.1^{3,18}.1^{5,16}.1^{22,33}.0^{2,19}.0^{4,17}.0^{6,15}.0^{8,13}.0^{21,34}.0^{22,33}.0^{25,30}]octatriaconta-6(15),7,9,11,13,23(33),25,27,29,30-decaene-2,19-dicarboxylic anhydride (**11yo**).* Reaction time 48 h; Yield 68%; mp>400 °C ($CHCl_3$); IR (KBr, cm^{-1}) 1790 (s), 1406 (s), 1197 (s), 1115 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 4H), 4.46 (s, 4H), 3.72 (s, 6H), 3.35 (s, 6H), 3.21 (s, 4H), 2.23 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0 (s), 150.0 (s), 141.2 (s), 139.6 (s), 128.3 (d), 112.3 (s), 79.8 (d), 73.5 (s), 72.0 (s), 53.8 (d), 52.4 (q), 52.2 (q), 19.9 (q); MS (FAB$^+$) *m*/*z* (%) 885 (M$^+$+H+4, 14), 883 (M$^+$+H+2, 23), 881 (M$^+$+H, 18), 315 (100), 301 (49), 242 (31); HRMS (FAB$^+$) Calcd for $C_{42}H_{37}Cl_4N_4O_9$ (M$^+$+H): 881.1315. Found: 881.1322.

*4.2.5.3. 7,18,28,39-Tetraaza-5,20,26,41-tetrachloro-45,45,46,46-tetramethoxy-43,44-dioxatetradecacyclo[22.18.1.1^{3,22}.1^{5,20}.1^{26,41}.0^{2,23}.0^{4,21}.0^{6,19}.0^{8,17}.0^{10,15}.0^{25,42}.0^{27,40}.0^{29,38}.0^{31,36}]hexatetraconta-6(19),7,9,11,13,15,17,27(40),28,30,32,34,36,38-tetradecaene-2,19-dicarboxylic anhydride (**11zo**).* Reaction time 48 h; Yield 78%; mp>400 °C ($CHCl_3$); IR (KBr, cm^{-1}) 1790 (s), 1403 (s), 1197 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 4H), 7.68 (dd, J_1=6.4 Hz, J_2=3.0 Hz, 4H), 7.34 (dd, J_1=6.4 Hz, J_2=3.0 Hz, 4H), 4.57 (s, 4H), 3.75 (s, 6H), 3.39 (s, 6H), 3.27 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9 (s), 151.7 (s), 138.4 (s), 132.6 (s), 127.9 (d), 127.1 (d), 126.4 (d), 111.1 (s), 80.0 (d), 73.4 (s), 72.1 (s), 53.9 (d), 52.5 (q), 52.3 (q); MS (FAB$^+$) *m*/*z* (%) 927 (M$^+$+H+4, 19), 926 (M$^+$+H+2, 16), 925 (M$^+$+H, 13); HRMS (FAB$^+$) Calcd for $C_{46}H_{33}Cl_4N_4O_9$ (M$^+$+H): 925.1002. Found: 925.1009.

*4.2.5.4. N-Phenyl-7,14,24,31-tetraaza-5,16,22,33-tetrachloro-37,37,38,38-tetramethoxy-35,36-dioxadodecacyclo[18.14.1.1^{3,18}.1^{5,16}.1^{22,33}.0^{2,19}.0^{4,17}.0^{6,15}.0^{8,13}.0^{21,34}.0^{22,33}.0^{25,30}]octatriaconta-6(15),7,9,11,13,23(33),25,27,29,30-decaene-2,19-dicarboximide (**11xa**).* Reaction time 30 h; Yield 78%; mp 355–356 °C (EtOH/$CHCl_3$); IR (KBr, cm^{-1}) (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–8.02 (m, 4H), 7.65–7.69 (m, 2H), 7.59–7.62 (m, 5H), 7.31–7.33 (m, 2H), 4.54 (s, 4H), 3.72 (s, 6H), 3.35 (s, 6H), 3.32 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5 (s), 151.2 (s), 142.6 (s), 130.7 (s), 130.1 (d), 130.0 (d), 129.6 (d), 129.3 (d), 126.4 (d), 112.6 (s), 79.6 (d), 72.1 (s), 71.1 (s), 54.3 (d), 52.4 (q), 52.1 (q); MS (FAB$^+$) *m*/*z* (%) 904 (M$^+$+H+4, 23), 902 (M$^+$+H+2, 30), 900 (M$^+$+H, 22), 663 (22), 460 (60), 307 (100), 273 (51), 165 (88); HRMS (FAB$^+$) Calcd for $C_{44}H_{34}Cl_4N_5O_8$ (M$^+$+H): 900.1156. Found: 900.1163.

*4.2.5.5. N-Phenyl-7,14,24,31-tetraaza-5,16,22,33-tetrachloro-37,37,38,38-tetramethoxy-10,11,27,28-tetramethyl-35,36-dioxadodecacyclo[18.14.1.1^{3,18}.1^{5,16}.1^{22,33}.0^{2,19}.0^{4,17}.0^{6,15}.0^{8,13}.0^{21,34}.0^{22,33}.0^{25,30}] octatriaconta-6(15),7,9,11,13,23(33),25,27,29,30-decaene-2,19-dicarboximide (**11ya**).* Reaction time 48 h; Yield 78%; mp 355–358 °C (EtOH/$CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 4H), 7.64–7.67 (m, 2H), 7.57–7.63 (m, 1H), 7.30–7.32 (m, 2H), 4.45 (s, 4H), 3.74 (s, 6H), 3.39 (s, 6H), 3.27 (s, 4H), 2.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5 (s), 150.2 (s), 141.3 (s), 139.8 (s), 130.8 (s), 130.0 (d), 128.6 (d), 126.4 (d), 112.6 (s), 79.6 (d), 72.1 (d), 71.1 (d), 54.2 (d), 52.4 (q), 52.1 (q), 20.0 (q); MS (FAB$^+$) *m*/*z* (%) 960 (M$^+$+H+4, 13), 958 (M$^+$+H+2, 21), 956 (M$^+$+H, 13), 663 (11), 460 (21), 289 (94), 71 (84); HRMS (FAB$^+$) Calcd for $C_{48}H_{42}Cl_4N_5O_8$ (M$^+$+H): 956.1782. Found: 956.1782.

*4.2.5.6. N-Phenyl-7,18,28,39-tetraaza-5,20,26,41-tetrachloro-45,45,46,46-tetramethoxy-43,44-dioxatetradecacyclo[22.18.1.1^{3,22}.1^{5,20}.1^{26,41}.0^{2,23}.0^{4,21}.0^{6,19}.0^{8,17}.0^{10,15}.0^{25,42}.0^{27,40}.0^{29,38}.0^{31,36}]hexatetraconta-6(19),7,9,11,13,15,17,27(40),28,30,32,34,36,38-tetradecaene-2,23-dicarboximide (**11za**).* Reaction time 72 h; Yield 65%; mp 383–384 °C (EtOH/$CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 4H), 7.79–7.82 (m, 4H), 7.66–7.68 (m, 2H), 7.38–7.41 (m, 4H), 7.32–7.34 (m, 2H), 4.59 (s, 4H), 3.76 (s, 6H), 3.39 (s, 6H), 3.31 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4 (s), 151.8 (s), 138.4 (s), 132.4 (s), 130.8 (s), 130.0 (d), 127.8 (d), 127.1 (d), 126.4 (d), 126.2 (d), 111.2 (s), 79.6 (d), 72.2 (d), 70.8 (d), 54.2 (d), 52.5 (q), 52.1 (q); MS (FAB$^+$) *m*/*z* (%) 1004 (M$^+$+H+4, 8), 1002 (M$^+$+H+2, 11), 1000 (M$^+$+H, 10), 899 (10), 337 (65), 323 (43), 77 (85); HRMS (FAB$^+$) Calcd for $C_{52}H_{38}Cl_4N_5O_8$ (M$^+$+H): 1000.1469. Found: 1000.1472.

*4.2.5.7. N-(4-Methoxyphenyl)-7,14,24,31-tetraaza-5,16,22,33-tetrachloro-37,37,38,38-tetramethoxy-35,36-dioxadodecacyclo[18.14.1.1^{3,18}.1^{5,16}.1^{22,33}.0^{2,19}.0^{4,17}.0^{6,15}.0^{8,13}.0^{21,34}.0^{22,33}.0^{25,30}]octatriaconta-6(15),7,9,11,13,23(33),25,27,29,30-decaene-2,19-dicarboximide (**11xb**).* Reaction time 36 h; Yield 82%; mp>410 °C ($CHCl_3$/EtOH); IR (KBr, cm^{-1}) 1718 (s), 1519 (m), 1193 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, 4H, J_1=6.3 Hz, J_2=3.5 Hz), 7.62 (dd, 4H, J_1=6.3 Hz, J_2=3.5 Hz), 7.24 (d, 2H, J=8.8 Hz), 7.16 (d, 2H, J=8.8 Hz), 4.52 (s, 4H), 3.92 (s, 3H), 3.75 (s, 6H), 3.34 (s, 6H), 3.30 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7 (s), 160.5 (s), 151.1 (s), 142.5 (s), 129.5 (d), 129.2 (d), 127.5 (d), 123.0 (s), 115.2 (d), 112.5 (s), 79.5 (d), 72.0 (s), 70.9 (s), 55.6 (q), 54.2 (d), 52.3 (q), 52.0 (q); MS (FAB$^+$) *m*/*z* (%) 933 (M$^+$+4, 6), 932 (M$^+$+3, 7), 930 (M$^+$+H, 5); HRMS (FAB$^+$) Calcd for $C_{45}H_{36}Cl_4N_5O_9$ (M$^+$+H): 930.1262. Found: 930.1263. Anal. Calcd for $C_{45}H_{35}Cl_4N_5O_9$: C, 58.02; H, 3.79; N, 7.52; O, 15.46. Found: C, 57.90; H, 3.75; N, 7.58; O, 15.41.

*4.2.5.8. N-(4-Methoxyphenyl)-7,14,24,31-tetraaza-5,16,22,33-tetrachloro-37,37,38,38-tetramethoxy-10,11,27,28-tetramethyl-35,36-dioxadodecacyclo[18.14.1.1^{3,18}.1^{5,16}.1^{22,33}.0^{2,19}.0^{4,17}.0^{6,15}.0^{8,13}.0^{21,34}.0^{22,33}.0^{25,30}]octatriaconta-6(15),7,9,11,13,23(33),25,27,29,30-decaene-2,19-dicarboximide (**11yb**).* Reaction time 24 h; Yield 83%; mp>410 °C ($CHCl_3$/EtOH); IR (KBr, cm^{-1}) 1722 (s), 1503 (s), 1208 (s), 1117(s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 4H), 7.28 (d, 2H, J=8.0 Hz), 7.16 (d, 2H, J=8.0 Hz), 4.42 (s, 4H), 4.01 (s, 3H), 3.76 (s, 6H), 3.34 (s, 6H), 3.21 (s, 4H), 2.38 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8 (s), 160.6 (s), 150.2 (s), 141.3 (s), 140.0 (s), 128.6 (d), 127.6 (d), 123.2 (s), 115.3 (d), 112.6 (s), 79.5 (d), 72.1 (s), 70.9 (s), 55.7 (q), 54.2 (d), 52.4 (q), 52.1 (q), 20.0 (q); MS (FAB$^+$) *m*/*z* (%) 988 (M$^+$+H+2, 30), 987 (M$^+$+2, 19), 986 (M$^+$+H, 22), 985 (M$^+$, 19), 930 (12), 315 (32), 136 (100); HRMS (FAB$^+$) Calcd for $C_{49}H_{44}O_9N_5Cl_4$ (M$^+$+H): 986.1888. Found: 986.1889; Anal. Calcd for $C_{49}H_{43}N_5O_9Cl_4$: C, 59.58; H, 4.39; N, 7.09; O, 14.58. Found: C, 60.08; H, 4.22; N, 7.20; O, 14.92.

4.2.5.9. N-(4-Methoxyphenyl)-7,18,28,39-tetraaza-5,20,26,41-tetrachloro-45,45,46,46-tetramethoxy-43,44-dioxatetradecacyclo[22.18.1.

*$1^{3,22}.1^{5,20}.1^{26,41}.0^{2,23}.0^{4,21}.0^{6,19}.0^{8,17}.0^{10,15}.0^{25,42}.0^{27,40}.0^{29,38}.0^{31,36}$]hexatetraconta-6(19),7,9,11,13,15,17,27(40),28,30,32,34,36,38-tetradecaene-2,23-dicarboximide (**11zb**).* Reaction time 24 h; Yield 83%; mp>410 °C ($CHCl_3$/EtOH); IR (KBr, cm^{-1}) 1722 (s), 1195 (s), 1105 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 4H), 7.81 (dd, 4H, J_1=6.4 Hz, J_2=3.2 Hz), 7.34 (dd, 4H, J_1=6.4 Hz, J_2=3.2 Hz), 7.29 (d, 2H, J=8.0 Hz), 7.12 (d, 2H, J=8.0 Hz), 4.59 (s, 4H), 3.92 (s, 3H), 3.79 (s, 6H), 3.39 (s, 6H), 3.28 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7 (s), 160.6 (s), 152.0 (s), 138.8 (s), 133.0 (s), 127.6 (d), 127.5 (d), 126.6 (d), 123.2 (s), 115.3 (d), 111.4 (s), 79.6 (d), 72.1 (s), 70.8 (s), 55.7 (q), 54.3 (d), 52.5 (q), 52.2 (q); MS (FAB^+) m/z (%) 1032 (M^++H+2, 20), 1030 (M^++H, 16), 664 (40), 663 (45), 307 (60); HRMS (FAB^+) Calcd for $C_{53}H_{40}Cl_4N_5O_9$ (M^++H): 1030.1575. Found: 1030.1593; Anal. Calcd for $C_{53}H_{39}Cl_4N_5O_9$: C, 61.70; H, 3.81; N, 6.79; O, 13.96. Found: C, 61.47; H, 3.51; N, 6.75; O, 14.05.

*4.2.5.10. N-(4-Hydroxyphenyl)-7,14,24,31-tetraaza-5,16,22,33-tetrachloro-37,37,38,38-tetramethoxy-35,36-dioxadodecacyclo[18.14.1.1^{3,18}.1^{5,16}.1^{22,33}.0^{2,19}.0^{4,17}.0^{6,15}.0^{8,13}.0^{21,34}.0^{22,33}.0^{25,30}]octatriaconta-6(15),7,9,11,13,23(33),25,27,29,30-decaene-2,19-dicarboximide (**11xc**).* Reaction time 36 h; Yield 88%; mp>410 °C ($CHCl_3$/hexane); IR (KBr, cm^{-1}) 3423 (br), 1718 (s), 1193 (s), 1119 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, 4H, J_1=6.3 Hz, J_2=3.4 Hz), 7.63 (dd, 4H, J_1=6.3 Hz, J_2=3.4 Hz), 7.18 (d, 2H, J=8.7 Hz), 7.09 (d, 2H, J=8.7 Hz), 6.72 (s, 1H), 4.52 (s, 4H), 3.74 (s, 6H), 3.34 (s, 6H), 3.29 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8 (s), 157.1 (s), 151.2 (s), 142.6 (s), 129.6 (d), 129.2 (d), 127.8 (d), 123.1 (s), 116.8 (d), 112.6 (s), 79.6 (d), 72.1 (s), 71.0 (s), 54.3 (d), 52.5 (q), 52.2 (q); MS (FAB^+) m/z (%) 918 (M^++H+2, 1), 916 (M^++H, 1), 307 (10), 77 (27); HRMS (FAB^+) Calcd for $C_{44}H_{34}Cl_4N_5O_9$ (M^++H): 916.1105. Found: 916.1107.

*4.2.5.11. N-(4-Hydroxyphenyl)-7,14,24,31-tetraaza-5,16,22,33-tetrachloro-37,37,38,38-tetramethoxy-10,11,27,28-tetramethyl-35,36-dioxadodecacyclo[18.14.1.1^{3,18}.1^{5,16}.1^{22,33}.0^{2,19}.0^{4,17}.0^{6,15}.0^{8,13}.0^{21,34}.0^{22,33}.0^{25,30}]octatriaconta-6(15),7,9,11,13,23(33),25,27,29,30-decaene-2,19-dicarboximide (**11yc**).* Reaction time 36 h; Yield 85%. Mp>400 °C ($CHCl_3$/hexane); IR (KBr, cm^{-1}) 3478 (br), 1770 (m), 1720 (s), 1506 (s), 1196 (s), 1114 (s); MS (FAB^+) m/z (%) 975 (M^++H+2, 32), 973 (M^++H, 28), 315 (100), 301 (56), 77 (45); compound **11yc** was characterized by the corresponding acetate derivative obtained by treatment with acetic anhydride. ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 4H), 7.37 (d, 2H, J=8.4 Hz), 7.31 (d, 2H, J=8.4 Hz), 4.47 (s, 4H), 3.71 (s, 6H), 3.35 (s, 6H), 3.21 (s, 4H), 2.37 (s, 3H), 2.27 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3 (s), 168.8 (s), 151.4 (s), 150.1 (s), 141.2 (s), 139.6 (s), 127.9 (d), 128.3 (d), 128.0 (s), 127.4 (d), 123.2 (d), 112.4 (s), 79.5 (q), 72.0 (s), 70.9 (s), 54.1 (d), 52.4 (q), 52.0 (q), 21.1 (q), 19.9 (q); MS (FAB^+) m/z (%) 1015 (M^++H+1, 40), 1014 (M^++H, 44); HRMS (FAB^+) Calcd for $C_{50}H_{44}Cl_4N_5O_{10}$ (M^++H): 1014.1837. Found: 1014.1845.

*4.2.5.12. N-(4-Hydroxyphenyl)-7,18,28,39-tetraaza-5,20,26,41-tetrachloro-45,45,46,46-tetramethoxy-43,44-dioxatetradecacyclo[22.18.1.1^{3,22}.1^{5,20}.1^{26,41}.0^{2,23}.0^{4,21}.0^{6,19}.0^{8,17}.0^{10,15}.0^{25,42}.0^{27,40}.0^{29,38}.0^{31,36}]hexatetraconta-6(19),7,9,11,13,15,17,27(40),28,30,32,34,36,38-tetradecaene-2,23-dicarboximide (**11zc**).* Reaction time 36 h; Yield 90%; mp>400 °C; IR (KBr, cm^{-1}) 3478 (br), 1720 (s), 1196 (s). MS (FAB^+) m/z (%) 1018 (M^++H+2, 4), 289 (10); compound **11zc** was characterized by the corresponding acetate derivative obtained by treatment with acetic anhydride. IR (KBr, cm^{-1}) 1770 (w), 1720 (s), 1645 (m), 1507 (s), 1196 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 4H), 7.58–7.59 (m, 4H), 7.34–7.40 (m, 4H), 7.26–7.29 (m. 4H), 4.66 (s, 4H), 3.75 (s, 6H), 3.40 (s, 6H), 3.27 (s, 4H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2 (s), 168.9 (s), 151.9 (s), 151.4 (s), 138.6 (s), 132.7 (s), 127.9 (d), 127.4 (d), 127.3 (d), 126.4 (d), 123.2 (d), 111.3 (s), 109.8 (s), 79.6 (d), 72.1 (s), 70.8 (s), 54.2 (q), 52.5 (q), 51.2 (q), 21.2 (q); MS (FAB^+) m/z (%) 1059 (M^++H+1, 8), 1058 (M^++H, 8); HRMS (FAB^+) Calcd for $C_{54}H_{40}Cl_4N_5O_{10}$ (M^++H): 1058.1524. Found: 1058.1548.

*4.2.5.13. N-(4-Methoxybenzyl)-7,14,24,31-tetraaza-5,16,22,33-tetrachloro-37,37,38,38-tetramethoxy-35,36-dioxadodecacyclo[18.14.1.1^{3,18}.1^{5,16}.1^{22,33}.0^{2,19}.0^{4,17}.0^{6,15}.0^{8,13}.0^{21,34}.0^{22,33}.0^{25,30}]octatriaconta-6(15),7,9,11,13,23(33),25,27,29,30-decaene-2,19-dicarboximide (**11xd**).* Reaction time 48 h; Yield 74%; mp>400 °C ($CHCl_3$); IR (KBr, cm^{-1}) 1708 (s), 1196 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, J_1=6.3 Hz, J_2=3.5 Hz, 4H), 7.57 (dd, J_1=6.3 Hz, J_2=3.5 Hz, 4H), 7.53 (d, J=8.7 Hz, 2H), 7.00 (d, J=8.7 Hz, 2H), 4.71 (s, 2H), 4.40 (s, 4H), 3.85 (s, 3H), 3.44 (s, 6H), 3.26 (s, 6H), 2.90 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9 (s), 159.7 (s), 151.4 (s), 142.3 (s), 130.8 (d), 129.1 (d), 128.8 (d), 126.8 (s), 114.6 (d), 112.1 (s), 79.4 (d), 72.1 (s), 70.8 (s), 55.3 (q), 53.7 (d), 52.2 (q), 51.9 (q), 42.4 (t); MS (FAB^+) m/z (%) 946 (M^++H+2, 30), 945 (M^++2, 14), 944 (M^++H, 26); HRMS (FAB^+) Calcd for $C_{46}H_{38}Cl_4N_5O_9$ (M^++H): 944.1418. Found: 944.1446; Anal. Calcd for $C_{46}H_{37}Cl_4N_5O_9$: C, 58.23; H, 3.94; N, 7.41; O, 15.23. Found: 57.92; H, 3.85; N, 7.49; O, 15.30.

*4.2.5.14. N-(4-Methoxybenzyl)-7,14,24,31-tetraaza-5,16,22,33-tetrachloro-37,37,38,38-tetramethoxy-10,11,27,28-tetramethyl-35,36-dioxadodecacyclo[18.14.1.1^{3,18}.1^{5,16}.1^{22,33}.0^{2,19}.0^{4,17}.0^{6,15}.0^{8,13}.0^{21,34}.0^{22,33}.0^{25,30}]octatriaconta-6(15),7,9,11,13,23(33),25,27,29,30-decaene-2,19-dicarboximide (**11yd**).* Reaction time 48 h; Yield 60%; mp>400 °C ($CHCl_3$); IR (KBr, cm^{-1}) 1709 (s), 1196 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 4H), 7.52 (d, J=8.7 Hz, 2H), 6.99 (d, J=8.7 Hz, 2H), 4.68 (s, 2H), 4.32 (s, 4H), 3.84 (s, 3H), 3.44 (s, 6H), 3.27 (s, 6H), 2.84 (s, 4H), 2.25 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0 (s), 159.6 (s), 150.5 (s), 141.1 (s), 139.5 (s), 130.8 (d), 128.4 (d), 126.8 (s), 114.6 (d), 112.2 (s), 79.4 (d), 72.1 (s), 70.8 (s), 55.3 (q), 53.6 (d), 52.2 (q), 51.9 (q), 42.4 (t); MS (FAB^+) m/z (%) 1004 (M^++H+4, 22), 1002 (M^++H+2, 36), 1000 (M^++H, 26), 999 (M^+, 5), 663 (12), 315 (47), 307 (31), 289 (24), 154 (100); HRMS (FAB^+) Calcd for $C_{50}H_{46}Cl_4N_5O_9$ (M^++H): 1000.2044. Found: 1000.2048; Anal. Calcd for $C_{50}H_{45}Cl_4N_5O_9$: C, 59.95; H, 4.53; N, 6.99; O, 14.37. Found: C, 59.84; H, 4.26; N, 7.17; O, 14.07.

*4.2.5.15. N-(4-Methoxybenzyl)-7,18,28,39-tetraaza-5,20,26,41-tetrachloro-45,45,46,46-tetramethoxy-43,44-dioxatetradecacyclo[22.18.1.1^{3,22}.1^{5,20}.1^{26,41}.0^{2,23}.0^{4,21}.0^{6,19}.0^{8,17}.0^{10,15}.0^{25,42}.0^{27,40}.0^{29,38}.0^{31,36}]-hexatetraconta-6(19),7,9,11,13,15,17,27(40),28,30,32,34,36,38-tetradecaene-2,23-dicarboximide (**11zd**).* Reaction time 48 h; Yield 72%; mp>400 °C ($CHCl_3$); IR (KBr, cm^{-1}) 1708 (s), 1516 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 4H), 7.55 (d, J=8.7 Hz, 2H), 7.35 (dd, J_1=6.1 Hz, J_2=3.0 Hz, 4H), 7.14 (dd, J_1=6.1 Hz, J_2=3.0 Hz, 4H), 7.02 (d, J=8.7 Hz, 2H), 4.72 (s, 2H), 4.60 (s, 4H), 3.86 (s, 3H), 3.49 (s, 6H), 3.35 (s, 6H), 2.89 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8 (s), 159.7 (s), 152.1 (s), 138.3 (s), 132.4 (s), 130.8 (d), 127.8 (d), 127.0 (d), 126.9 (s), 126.1 (d), 114.6 (d), 110.9 (s), 79.5 (d), 72.2 (s), 70.7 (s), 55.3 (q), 53.8 (d), 52.3 (q), 52.0 (q), 42.5 (t); MS (FAB^+) m/z (%) 1046 (M^++H+2, 100), 1045 (M^++2, 55), 1044 (M^++H, 73); HRMS (FAB^+) Calcd for $C_{54}H_{42}Cl_4N_5O_9$ (M^++H): 1044.1731. Found: 1044.1727; Anal. Calcd for $C_{54}H_{41}Cl_4N_5O_9$: C, 62.02; H, 3.95; N, 6.70; O, 13.77. Found: C, 61.57; H, 4.17; N, 6.93; O, 13.43.

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21. Alternative modes of dimeric self-assembly, **I** and **J**, appear to be inexplicable for the upfield shift of the oxa-bridgehead methine protons (H_a).
22. Crystallographic data (excluding structure factors) for **11xa**, **11yd**, **11zb**, and **11zd** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 741980, CCDC 741981, CCDC 741982, and CCDC 741983, respectively.
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