JOC The Journal of Organic Chemistry

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Quinoxaline-Based Cyclo(oligophenylenes)

Lidia Marin,[†,‡] Julija Kudrjasova,[†,‡] Pieter Verstappen,[†,‡] Huguette Penxten,[†,‡] Koen Robeyns,[§] Laurence Lutsen,[†,‡] Dirk J. M. Vanderzande,[†,‡] and Wouter Maes*[,†,‡]

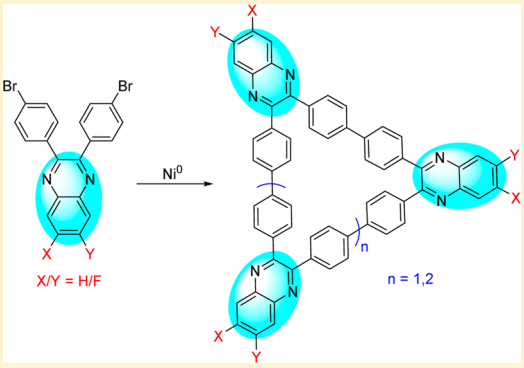
[†]Design & Synthesis of Organic Semiconductors (DSOS), Institute for Materials Research (IMO-IMOMEC), Hasselt University, Agoralaan 1-Building D, 3590 Diepenbeek, Belgium

[‡]IMOMEC Ass. Lab., IMEC, Universitaire Campus-Wetenschapspark 1, 3590 Diepenbeek, Belgium

[§]Institute of Condensed Matter and Nanosciences (IMCN), Université catholique de Louvain (UCL), Bâtiment Lavoisier, Place Louis Pasteur 1, 1348 Louvain-la-Neuve, Belgium

Supporting Information

ABSTRACT: A series of fully conjugated quinoxaline-based oligophenylene macrocycles is synthesized by Ni^0-mediated Yamamoto-type diaryl homocoupling of (fluorinated) 2,3-bis(4′-bromophenyl)quinoxaline precursors. Cyclotrimers and cyclotetramers are obtained as the dominant reaction products. The cyclooligomers are fully characterized, including single-crystal X-ray structures, and their optoelectronic properties are analyzed with respect to possible applications in host–guest chemistry and organic electronics.



Advanced "shape-persistent" macrocyclic compounds built from rigid (aromatic) building blocks, interconnected in such a way that the final structure cannot collapse, have been widely explored in the past couple of years.[1−3] Among these, fully π-conjugated carbon nanorings composed of 1,4-connected phenyl units—known as [*n*]CPPs (cycloparaphenylenes), with *n* denoting the number of phenyl rings in the macrocycle—are of particular interest for optoelectronic applications and host–guest chemistry (e.g., fullerene binding).[4−10] Because their electro-optical and supramolecular (assembly) properties are strongly dependent on the size (of the cavity), continuous synthetic efforts have focused on variation and control over the diameter of the "carbon nanohoops". [*n*]CPPs represent the shortest sidewall segment of armchair carbon nanotubes and can serve as a scaffold for the controlled growth of fully sp^2-hybridized carbon structures. For this reason, ways of expanding and interconnecting CPP units, for instance by arene bridges, are also being actively pursued.[11−13] On the other hand, the introduction of other (hetero)aryl moieties can strongly influence the shape of the macrocycles, the π–π stacking properties, the HOMO–LUMO energy levels, and the molecular interactions.[14−17] Additionally, when some of the (hetero)aromatic rings are interconnected via the ortho positions, the cavity loses its circular shape and adopts a triangular conformation (releasing ring strain).[18−21] Most fully conjugated macrocyclic systems present a significant synthetic challenge. Synthesis protocols toward cyclic oligophenylenes are generally based on transition metal-mediated cross-coupling reactions, e.g., reaction of aryl Grignard/lithium reagents with $CuCl_2$ or homocoupling of aryl halides by electron transfer oxidation of Lipshutz cuprates, producing cyclic products with varying degrees of selectivity (over other macrocycles and open-chain analogues).[1−21]

Quinoxaline heterocycles have been applied on multiple occasions as building blocks for the development of macrocyclic molecular receptors[22,23] as well as new semiconducting materials,[24−30] introducing electron deficient character and allowing structural fine-tuning (e.g., extension of the chromophore and introduction of solubilizing side chains at positions 2 and 3). Push–pull copolymers incorporating quinoxalines as the acceptor parts have recently afforded high power conversion efficiencies in organic solar cells.[24−29] On the other hand, a quinoxaline-based poly(arylene ethynylene) copolymer was applied as a chemosensor for explosive detection, with high fluorescence quenching sensitivity toward TNT.[30]

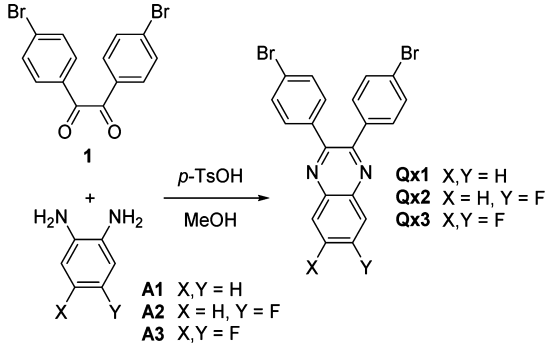
Herein, we report on the synthesis and characterization of a small family of ortho/para-linked nona- and dodecaphenylene macrocycles via Ni^0-mediated cyclooligomerization of 4′-bromophenyl-functionalized quinoxaline precursors. The quinoxaline heterocycles introduce π-acceptor character into the regular cyclic oligophenylene framework. The "monomers" **Qx1−3** used in these transformations were prepared in high yields (79–94%) by acid-mediated condensation between 1,2-bis(4′-bromophenyl)ethane-1,2-dione (**1**) and the correspond-

Received: December 8, 2014
Published: January 22, 2015

DOI: 10.1021/jo502771a
J. Org. Chem. 2015, 80, 2425−2430

ing diamines (**A1−3**) (Scheme 1).[31] The introduction of fluorine atoms at positions 6 and/or 7 is used as a (proof-of-concept) tool for fine-tuning the energy levels[28,32,33] and allows further elaboration of the final cyclooligomers by nucleophilic aromatic substitution reactions.[34,35]

Scheme 1. Synthesis of Quinoxaline Monomers Qx1−3



At the monomer stage, the presence of the bromine atoms in the para positions of the 2,3-phenyl groups allows to use these derivatives in Ni^0-mediated transformations (less toxic and less expensive than the Pd variants). Yamamoto homocoupling of quinoxaline monomers **Qx1−3** can give rise to cyclic structures and/or polymeric materials.[13,20,36−38] At first, **Qx1** was treated with $Ni(cod)_2$ (in the presence of 2,2′-bipyridine and 1,5-cyclooctadiene) in a DMF/toluene mixture and reacted for 3 days at 95 °C (slightly modified compared to the standard conditions used for Ni^0-mediated polymerizations[13,20,31,36−38]). The resulting crude material was purified by preparative size exclusion chromatography (prep-SEC). Cyclotrimer **CT3-1** (related to the regular *o,p,p,o,p,p,o,p,p*-nonaphenylene[18,19]) was isolated as the major product in 35% yield, as analyzed by NMR and (HR)MS analysis, together with a smaller amount of the analogous cyclotetramer **CT4-1** in 13% yield, pointing to a bias for the reaction to produce the smallest achievable macrocycles (Scheme 2). The SEC profile of the crude reaction mixture showed that the formation of (cyclo)oligomers and/or polymers with molar masses superior to 1000 Da was modest (Figure S1 of the Supporting Information). Additionally, the monomer seemed to be completely consumed in the transformation. Initial confusion between cyclodimers and cyclotetramers (caused by the appearance of *m*/2 signals in the ESI-MS spectra) was countered by the prep-SEC results, the second products being "larger" (in hydrodynamic volume) than the cyclotrimers (i.e., eluting first). Later, MALDI-TOF allowed clearer monitoring of the cyclooligomerization mixture as well as the isolated components (see the Supporting Information). Final confirmation was obtained by X-ray single-crystal analysis (*vide infra*).

The simple and concise synthetic protocol was then extended to fluorinated monomers **Qx2** and **Qx3**, affording similar results (Scheme 2). All macrocycles were obtained in pure form (**CT3-2** and **CT4-2** as a mixture of regioisomers) and showed reasonable to good solubility (e.g., in chlorinated organic solvents), allowing full structural characterization. In an effort to increase the macrocycle yield, a high-dilution protocol favoring intramolecular cyclization was applied. The obtained results were, however, similar (slightly inferior) to those of the original approach (28 and 7% yields of **CT3-1** and **CT4-1**, respectively).

Single crystals suitable for X-ray analysis were grown from $CHCl_3$ for **CT3-1** (Figure 1) and **CT4-3** (Figure 2), confirming the structures and illustrating the solid-state conformations.[39] The equilateral triangular structure of **CT3-1** has sides of

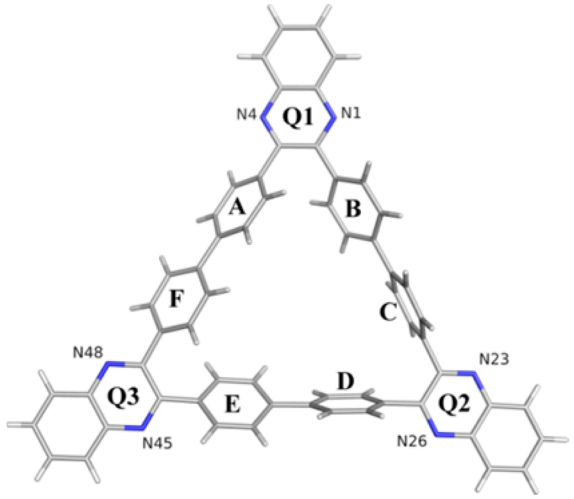
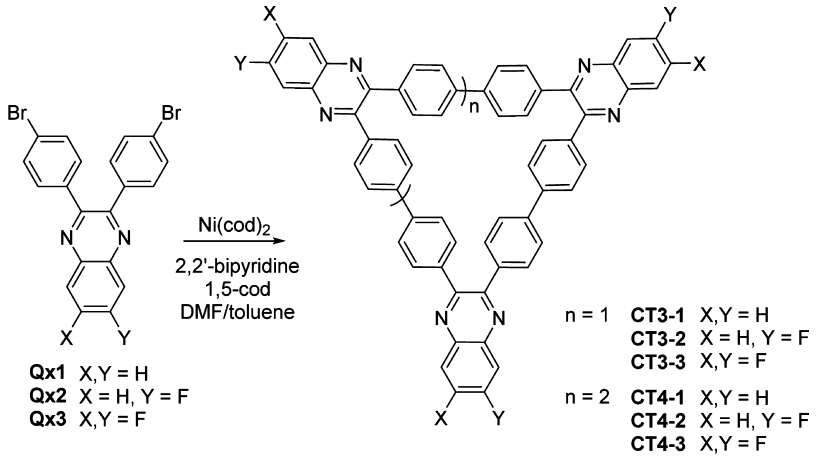


Figure 1. Stick representation of the X-ray structure of **CT3-1**, with the labeling scheme for the quinoxaline (Q) and phenyl rings.

Scheme 2. Yamamoto Cyclooligomerization Protocol toward Quinoxaline-Based Cyclic Oligoarylenes



DOI: 10.1021/jo502771a
J. Org. Chem. 2015, 80, 2425−2430

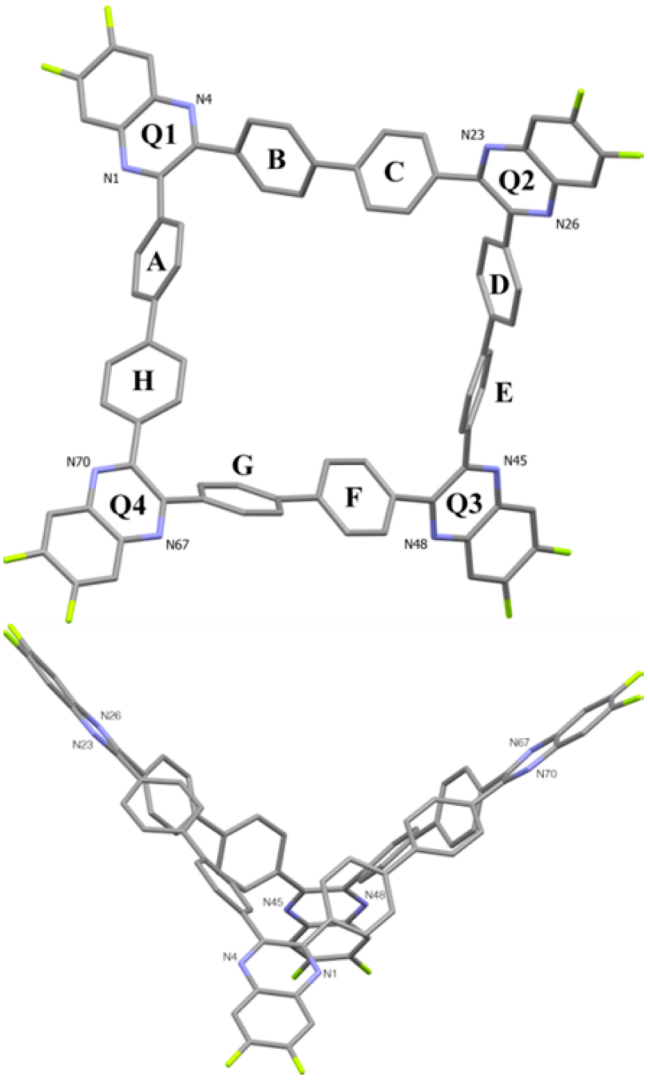


Figure 2. Stick representation of the X-ray structure of **CT4-3**, with the labeling scheme for the quinoxaline (Q) and phenyl rings.

~12.78 Å, as measured between the centroids of the pyrazine rings (Figure S13 of the Supporting Information). The three quinoxalines are situated in the same plane with a maximal deviation for C7 of 0.2027(26) Å from the plane calculated through all quinoxaline atoms (labeling scheme in Figure S12 of the Supporting Information). The bridging phenyl rings are inclined, and the angles between the quinoxaline plane and the phenyl rings are on the same order of magnitude for both phenyl rings attached to the same quinoxaline moiety [Q1−A, 51.57(7)°; Q1−B, 50.69(7)°; Q2−C, 88.36(8)°; Q2−D, 71.22(7)°; Q3−E, 43.57(8)°; Q3−F, 41.98(7)°], showing that the rotation of one phenyl ring will have a cascade effect on the other. This is a direct result of steric hindrance and is less pronounced when the phenyl rings are nearly perpendicular as around Q2 (Figure 1). The angles between the phenyl rings belonging to the same diphenyl linker are 33.16(8)° (A−F) and 30.91(14)° (B−C), which is close to the average value of 31.5° found in the CSD for twisted nonconjugated diphenyls. The third diphenyl (D−E) residue has an internal angle of 12.24(13)°. The latter "parallel" arrangement is a result of the crystal packing, as the D−E side of the triangle is in close contact (shortest distance of 3.387 Å) with a neighboring D−E side through an inversion center. This is accompanied by significant ring overlap (offset stacking) for the flanking quinoxalines (Q1 and Q3) with neighboring moieties (Figure S15 of the Supporting Information).

The **CT4-3** structure is not at all planar but shows a butterfly arrangement (Figure 2). As in the trigonal structure, the centroids of the pyrazine rings are separated by approximately the same distance, here on average 12.71 Å (Figure S14 of the Supporting Information), which is to be expected with the linear diphenyl linker. Looking at the inclination of the phenyl rings with respect to the quinoxaline moieties, one can see that, contrary to the triangular structure, similar inclinations are observed between two adjacent quinoxaline rings [Q1−B, 51.67(24)°; Q2−C, 51.35(25)°; Q2−D, 38.88(32)°; Q3−E, 41.85(33)°; Q3−F, 52.03(25)°; Q4−G, 44.55(32)°; Q4−H, 42.44(26)°; Q1−A, 31.24(42)°]. All internal diphenyl angles are similar [46.04(29)° (B−C), 40.43(24)° (D−E), 44.30(38)° (F−G), and 39.83(44)° (H−A)]. The crystal packing shows that the residues are found around a 2-fold screw axis, where the tetramers cradle 180° rotated residues that are stacked upon each other (Figure S16 of the Supporting Information). One might consider π-stacking interactions between Q1 and Q3 within a stack, but the ring overlap is not as pronounced as seen in the triangular structure.

To judge their appropriateness for applications in organic electronics (notably photovoltaics and light-emitting diodes), the optical and electrochemical properties of the macrocycles were analyzed (Table 1). The absorption features (Figure 3) are barely different within both cyclooligomer series (similar λ_{max} values and an evident increase in molar absorptivity for the cyclotetramers). The emission maxima (blue emission centered at ~425 nm, red-shifted with respect to the regular cyclic nona- and dodecaphenylenes[19]) are also quite similar (Figure 3), but there is a noticeable increase in fluorescence quantum yield (and concomitant excited-state lifetime) upon fluorination, up to an appreciable Φ_F value of 0.61 for **CT3-3**. Fluorescence quantum yields are somewhat lower for the cyclotetramers. Compared to regular cyclic oligophenylenes, the quinoxaline-

Table 1. Optical and Electrochemical Properties of the Synthesized Cyclooligomers

compd	$\lambda_{max,abs}$ (nm)	log ε (×10^3)	$\lambda_{max,PL}$ (nm)	ΔE_{opt}[a]	τ (ns)[b]	Φ_F	E^{ox}_{onset} (eV)	E_{HOMO} (eV)	E^{red}_{onset} (eV)	E_{LUMO} (eV)	ΔE_{ec} (eV)[c]	$E_{LUMO,calcd}$ (eV)[d]
CT3-1	281/366	4.757/4.639	424	2.98	0.53	0.44	1.53	−6.50	−1.96	−3.00	3.49	−3.52
CT3-2	280/369	4.923/4.822	427	2.97	0.62	0.52	1.55	−6.52	−1.85	−3.12	3.39	−3.55
CT3-3	280/369	4.936/4.866	428	2.99	0.67	0.61	1.59	−6.55	−1.84	−3.13	3.42	−3.56
CT4-1	297/366	4.985/4.939	420	2.97	0.31	0.22	1.39	−6.36	−1.87	−3.10	3.26	−3.39
CT4-2	298/375	4.949/4.966	424	2.97	0.49	0.41	1.47	−6.43	−1.83	−3.13	3.30	−3.46
CT4-3	285/370	5.134/5.162	425	2.99	0.60	0.44	1.48	−6.44	−1.78	−3.18	3.26	−3.45

[a]Optical HOMO−LUMO gap (film). [b]Fluorescence lifetime. [c]Electrochemical HOMO−LUMO gap. [d]$E_{LUMO,calcd} = E_{HOMO} + \Delta E_{opt}$.

DOI: 10.1021/jo502771a
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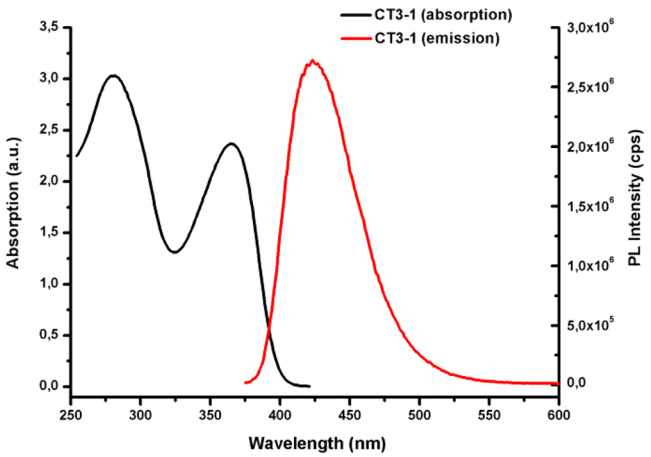

Figure 3. Absorption and emission spectra (in $CHCl_3$) of **CT3-1**.

based macrocycles have more π-acceptor character, which can be seen from the HOMO/LUMO values (based on the oxidation/reduction onset potentials as determined by cyclic voltammetry). The presence of the fluorine atoms has a weak influence on the frontier orbital energy levels, lowering both the HOMO and LUMO energies.[28,32,33] The cyclotetramers are oxidized somewhat more easily,[4−10,19] leading to slightly reduced electrochemical bandgaps.

In summary, triangular and butterfly-shaped fully π-conjugated cyclic oligophenylenes were readily prepared by a straightforward Ni-mediated biaryl coupling protocol employing suitably functionalized quinoxaline precursors. These derivatives, after proper extension of the conjugated system and/or variation of the substitution pattern, can be regarded as attractive (complexity-building) molecular platforms toward sophisticated organic architectures that can be applied in materials science, e.g., organic electronics, self-assembly and nanostructure formation, size-selective supramolecular chemistry (fullerene complexation[10,21,40] or explosive detection[19,30]), surface patterning,[41] and conjugated organic frameworks.[42]

EXPERIMENTAL SECTION

The Qx monomers were synthesized according to a previously reported procedure.[31]

2,3-Bis(4′-bromophenyl)quinoxaline (Qx1).[43,44] General Procedure 1. A mixture of *o*-phenylenediamine (**A1**) (2.50 g, 23.1 mmol), 1,2-bis(4′-bromophenyl)ethane-1,2-dione (**1**) (8.51 g, 23.1 mmol), and *p*-toluenesulfonic acid (*p*-TsOH) (0.44 g, 10 mol %) in methanol (150 mL) was reacted at reflux temperature for 6 h. The resulting mixture was allowed to cool to rt, and the precipitate was filtered off and washed with methanol. Recrystallization from THF afforded **Qx1** as pale-yellow crystals (9.51 g, 94%). The material identity and purity were confirmed by MS and ^{1}H NMR.[43,44]

2,3-Bis(4′-bromophenyl)-6-fluoroquinoxaline (Qx2).[45,46] General procedure 1 was used with 4-fluorobenzene-1,2-diamine (**A2**) (1.50 g, 11.9 mmol), 1,2-bis(4′-bromophenyl)ethane-1,2-dione (**1**) (4.38 g, 11.9 mmol), *p*-TsOH (0.23 g, 10 mol %), and methanol (100 mL) to produce white crystals (4.28 g, 79%): mp 157−159 °C; MS (ESI) $[M + H]^+$ calcd for $C_{20}H_{12}Br_2FN_2$ m/z 456.9, found m/z 456.9; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, J = 5.6/9.2 Hz, 1H), 7.76 (dd, J = 2.8/9.2 Hz, 1H), 7.59−7.54 (m, 1H), 7.50 (d, J = 8.8 Hz, 4H), 7.40−7.37 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.2 (164.4/161.9, d, $^1J_{CF}$ = 252 Hz), 152.8, 151.4 (151.40/151.37, d, $^5J_{CF}$ = 3 Hz), 142.1 (142.2/142.0, d, $^3J_{CF}$ = 13 Hz), 138.6, 137.5, 137.4, 131.9 (CH), 131.53 (CH), 131.47 (CH), 131.36 (CH), 124.1, 123.9, 121.0 (121.1/120.9, d, $^2J_{CF}$ = 26 Hz, CH), 112.8 (112.9/112.6, d, $^2J_{CF}$ = 22 Hz, CH).

2,3-Bis(4′-bromophenyl)-6,7-difluoroquinoxaline (Qx3).[47] General procedure 1 was used with 4,5-difluorobenzene-1,2-diamine (**A3**) (1.00 g, 6.94 mmol), 1,2-bis(4′-bromophenyl)ethane-1,2-dione (**1**) (2.55 g, 6.94 mmol), *p*-TsOH (0.13 g, 10 mol %), and methanol (80 mL) to produce white crystals (2.60 g, 79%): mp 167−169 °C; MS (ESI) $[M + H]^+$ calcd for $C_{20}H_{11}Br_2F_2N_2$ m/z 474.9, found m/z 474.9; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (t, J = 9.3 Hz, 2H), 7.51 (d, J = 8.8 Hz, 4H), 7.36 (d, J = 8.8 Hz, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 152.8 (154.2/154.0/151.6/151.4, dd, $^1J_{CF}$ = 258 Hz, $^2J_{CF}$ = 18 Hz), 152.2, 138.6 (138.70/138.63/138.57, t, J_{CF} = 6 Hz), 137.2, 131.9 (CH), 131.5 (CH), 124.2, 114.9 (114.97/114.91/114.85/114.78, dd, $^2J_{CF}$ = 13 Hz, $^3J_{CF}$ = 7 Hz, CH).

Macrocyclization. General Procedure 2. For the cyclooligomerization of monomer **Qx1**, $Ni(cod)_2$ (1.00 g, 3.64 mmol), 2,2′-bipyridine (0.57 g, 3.64 mmol), and DMF (12.5 mL) were placed in a Schlenk tube inside a glovebox. 1,5-Cyclooctadiene (0.66 g, 6.06 mmol), degassed by being bubbled through with N_2 gas for 20 min, was added, and the mixture, which developed a deep violet color, was vigorously stirred for 30 min at 85 °C. A solution of **Qx1** (0.670 g, 1.52 mmol) in degassed toluene (12.5 mL) was then added, and the mixture was allowed to react for 3 days at 95 °C. The resulting mixture was allowed to cool to rt; water was added, and the mixture was extracted with chloroform. The combined organic layers were dried over $MgSO_4$ and filtered over a Celite plug. Evaporation of the solvent under reduced pressure afforded an off-white solid that was purified by means of preparative SEC using chloroform as an eluent (portion wise; 20 mg of crude material in 3 mL of $CHCl_3$ to avoid precipitation). Two main fractions were recovered.

Cyclotetramer **CT4-1**: white solid (57 mg, 13%); HRMS (ESI-Orbitrap) $[M + 2H]^{2+}$ calcd for $C_{80}H_{50}N_8$ m/z 561.2079, found m/z 561.2074; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24−8.20 (m, 8H), 7.83−7.78 (m, 8H), 7.72 (d, J = 8.8 Hz, 16H), 7.62 (d, J = 8.8 Hz, 16H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 152.8, 141.51, 141.47, 138.3, 130.7 (CH), 130.3 (CH), 129.4 (CH), 127.4 (CH); FTIR υ_{max} 3053, 1343, 1260, 1218, 1061, 1019, 1006, 978, 827, 800, 761 cm^{-1}.

Cyclotrimer **CT3-1**: white solid (149 mg, 35%); HRMS (ESI-Orbitrap) $[M + H]^+$ calcd for $C_{60}H_{37}N_6$ m/z 841.3080, found m/z 841.3063; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25−8.22 (m, 6H), 7.84−7.81 (m, 6H), 7.67 (d, J = 8.0 Hz, 12H), 7.53 (d, J = 8.0 Hz, 12H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.7, 141.3, 139.7, 138.6, 130.4 (CH), 130.3 (CH), 129.4 (CH), 126.6 (CH); FTIR υ_{max} 3053, 1343, 1260, 1218, 1061, 1019, 1006, 980, 827, 760 cm^{-1}.

All macrocycles tend to decompose (as observed by a color change) before melting.

Cyclooligomerization of monomer **Qx2** (0.693 g, 1.51 mmol) was conducted according to general procedure 2.

Cyclotetramer **CT4-2** (mixture of regioisomers): white solid (77 mg, 17%); HRMS (ESI-Orbitrap) $[M + 2H]^{2+}$ calcd for $C_{80}H_{46}F_4N_8$ m/z 597.1891, found m/z 597.1916; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, J = 5.6/9.2 Hz, 4H), 7.82 (dd, J = 2.8/9.2 Hz, 4H), 7.73−7.68 (m, 16H), 7.61 (d, J = 8.0 Hz, 16H), 7.59−7.54 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.1 (164.4/161.9, d, $^1J_{CF}$ = 251 Hz), 153.5, 152.1, 142.2 (142.2/142.1, d, $^3J_{CF}$ = 13 Hz), 141.70/141.66/141.55/141.49, 138.7, 138.12/138.09/138.01/137.98, 131.5 (131.5/131.4, d, $^3J_{CF}$ = 10 Hz, CH), 130.6 (CH), 127.5 (CH), 120.8 (120.88/120.62, d, $^2J_{CF}$ = 26 Hz, CH), 112.8 (112.9/112.7, d, $^2J_{CF}$ = 22 Hz, CH); $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$) δ −109.00; FTIR υ_{max} 3053, 1620, 1607, 1480, 1343, 1218, 1207, 1156, 1114, 1060, 1019, 1006, 981, 960, 907, 866, 835, 797, 731 cm^{-1}.

Cyclotrimer **CT3-2** (mixture of regioisomers): white solid (186 mg, 41%); HRMS (ESI-Orbitrap) $[M + H]^+$ calcd for $C_{60}H_{34}F_3N_6$ m/z 895.2797, found m/z 895.2781; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, J = 5.6/9.2 Hz, 3H), 7.84 (dd, J = 2.8/9.2 Hz, 3H), 7.66 (d, J = 8.2 Hz, 12H), 7.62−7.57 (m, 3H), 7.51 (2xd, J = 8.2 Hz, 12H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 163.2 (164.8/161.5, d, $^1J_{CF}$ = 251 Hz), 154.5, 153.1, 142.1 (142.2/142.0, d, $^3J_{CF}$ = 13 Hz), 139.89/139.83/139.77/139.71, 138.5/138.4/138.3, 131.5 (131.5/131.4, d, $^3J_{CF}$ = 10 Hz, CH), 130.2 (CH), 126.6 (CH), 120.8 (120.9/120.6, d, $^2J_{CF}$ = 26 Hz, CH), 112.9 (113.0/112.7, d, $^2J_{CF}$ = 21 Hz, CH); $^{19}F\{^1H\}$ NMR

DOI: 10.1021/jo502771a
J. Org. Chem. 2015, 80, 2425−2430

(282 MHz, $CDCl_3$) δ −109.00; FTIR υ_{max} 3053, 1620, 1607, 1480, 1343, 1218, 1207, 1156, 1114, 1060, 1019, 1006, 982, 960, 866, 835, 747 cm^{-1}.

Cyclooligomerization of monomer **Qx3** (0.723 g, 1.52 mmol) was conducted according to general procedure 2.

Cyclotetramer **CT4-3**: white solid (60 mg, 12%); HRMS (ESI-Orbitrap) $[M + 2H]^{2+}$ calcd for $C_{80}H_{42}F_8N_8$ m/z 633.1702, found m/z 633.1709; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (t, J = 9.2 Hz, 8H), 7.69 (d, J = 8.6 Hz, 16H), 7.61 (d, J = 8.6 Hz, 16H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 152.8 (154.2/154.0/151.6/151.4, dd, $^1J_{CF}$ = 257 Hz, $^2J_{CF}$ = 18 Hz), 152.9, 141.7, 138.8, 137.9, 130.6 (CH), 127.5 (CH), 114.9 (115.02/114.91/114.86, CH); $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$) δ −130.66; FTIR υ_{max} 3053, 1607, 1498, 1353, 1343, 1218, 1196, 1175, 1144, 1059, 1019, 1006, 977, 873, 830, 788, 753 cm^{-1}.

Cyclotrimer **CT3-3**: white solid (117 mg, 24%); HRMS (ESI-Orbitrap) $[M + H]^+$ calcd for $C_{60}H_{31}F_6N_6$ m/z 949.2514, found m/z 949.2521; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (t, J = 9.2 Hz, 6H), 7.66 (d, J = 8.2 Hz, 12H), 7.50 (d, J = 8.2 Hz, 12H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 152.8 (154.1/153.9/151.6/151.4, dd, $^1J_{CF}$ = 257 Hz, $^2J_{CF}$ = 18 Hz), 153.9, 139.9, 138.6 (138.69/138.63/138.57, t, J_{CF} = 6 Hz), 138.1, 130.2 (CH), 126.7 (CH), 115.1 (115.13/115.06/115.01/114.95, dd, $^2J_{CF}$ = 12 Hz, $^3J_{CF}$ = 7 Hz, CH); $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$) δ −130.71; FTIR υ_{max} 3053, 1607, 1498, 1358, 1343, 1218, 1196, 1175, 1144, 1059, 1019, 1006, 979, 873, 830, 788, 750 cm^{-1}.

High-Dilution Procedure. The reaction was performed as described above (general procedure 2), but in this case, the solution of monomer **Qx1** (0.670 g, 1.52 mmol) in degassed toluene (12.5 mL) was added slowly over a period of 4 h using an automatic syringe pump. Workup and purification were conducted as reported above, affording the pure **CT3-1** (128 mg, 28%) and **CT4-1** (32 mg, 7%) macrocycles as white solids.

■ ASSOCIATED CONTENT

Supporting Information

General experimental methods, SEC profiles and ESI/MALDI-TOF mass spectra for the crude reaction mixtures, cyclic voltammograms, extra X-ray figures and data (and .cif files for **CT3-1** and **CT4-3**), and ^1H, ^{19}F, and ^{13}C NMR spectra for all novel macrocycles (with additional two-dimensional HETCOR spectra and full chemical shift assignments). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: wouter.maes@uhasselt.be.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Hasselt University for continuous financial support and BELSPO for supporting the IAP 7/05 network. We further acknowledge Hercules for providing the funding for the Orbitrap mass spectrometer.

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DOI: 10.1021/jo502771a
J. Org. Chem. 2015, 80, 2425−2430