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Synthesis of Cyclotriveratrylene–Phenylacetylene Derivatives and a Photophysical Investigation of Rigid Conjugated Cyclotriveratrylene Dendrimers

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Various functionalized host molecules and building blocks can be derived from the cone-shaped cyclotriveratrylene (CTV). In this article, we report on the synthesis of CTV-I_3 derivatives **3a** and **3b** and their Sonogashira cross-coupling with various terminal aryl-alkynes, to synthesize CTV-phenylacetylene derivatives in moderate to good yields. In this way, three star-like conjugated dendrimers with rigid macrocyclic cores **4k**–**m**, which showed good photophysical properties, were also synthesized. The band gaps of **4k**–**m** are 3.49, 3.49 and 3.45 eV, and the fluorescence quantum yields are 0.64, 0.78, 0.48 (2-aminopyridine as a standard and excited at 310 nm), respectively. Electrochemical studies revealed their HOMO and LUMO energy levels. Our research disclosed that these CTV dendrimers could potentially be used as host materials in OLEDs.

Introduction

The rigid, cone-shaped molecule of cyclotriveratrylene (CTV) is a macrocyclic host that has been investigated in detail in recent decades.[1] Numerous studies have been undertaken to synthesize CTV analogues.[2] In most cases, new CTV derivatives have been developed with etherification or esterification at the upper rims of cyclotricatechylene (CTC) and cyclotriguaiacylene (CTG), which gave flexible extended arms.[3] These CTV analogues possess deeper cavities and various functional groups. CTV and its derivatives have shown wide applications in fields such as host-guest chemistry,[4] organic or metallo-supramolecular assemblies,[5] ion-sensing,[6] and bio-sensing.[7]

The latest work disclosed that CTV analogues with rigid arms contain deeper cavities that provide unique advantages when constructing functional materials.[8] This stimulated our curiosity to synthesize CTV derivatives with even larger rigid cavities. The convenient synthetic strategy involving bromide-substituted reactant CTV-Br_3[9] makes it possible to prepare the rigid CTV derivatives through Suzuki–Miyaura coupling or Sonogashira coupling reactions. Recently, we have reported the use of classical Suzuki–Miyaura coupling conditions with CTV-Br_3 in the presence of [$Pd(PPh_3)_4$] and anhydrous K_2CO_3.[10] Reactions of phenyl, 4-tolyl, or 4-(ethoxycarbonyl)phenyl boronic acid with CTV-Br_3 did give the desired products, but the yields were far from satisfactory. Further study showed that the more reactive indolylphosphane ligand was required. Because the coupling reactivity of iodides are superior to bromides,[11] more reactive reactants such as iodide-substituted CTV were investigated. Collet reported the synthesis of CTV-I_3 in 1995.[12] However, its synthesis required many steps and harsh reaction conditions. Gosse[13] reported an efficient route to synthesize the same CTV-I_3 starting from 3-hydroxy-4-iodobenzoic acid in three steps with 47% overall yield. Due to the low solubility of this CTV-I_3, we replaced the methyl group with propyl or butyl groups and improved Gosse's procedures to obtain the CTV-I_3 derivatives **3a** and **3b**. A series of CTV-phenylacetylene derivatives were then obtained in moderate to good yields through Sonogashira cross-coupling from **3a** and **3b**.

Dendrimers are precisely defined, three-dimensional structures that combine properties of both polymers and nonpolymers. They are designed on the basis of the Cayley tree topology and are composed of repeating units that, overall, result in high overall molecular weight compounds, but are monodisperse, well-defined molecules. It is always important for the design of functional macromolecules to investigate their physical or chemical properties, which are affected by their molecular structure. Previous work showed that CTV functionalized with polybenzyl ether dendrons afforded an internal cavity with appropriate dimensions and shape for forming a 1:1 complex with C_{60}.[14] The K_a values of the complex increase significantly with the generation number of the surrounding dendritic substituents. Percec and co-workers reported a series of dendritic CTVs that

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self-assemble into a hexagonal columnar lattice and/or into chiral supramolecular spheres depending on the type of chiral dendrimer used.[15] On the other hand, Moore reported the first fluorescent phenylacetylene dendrimers.[16] Subsequently, numerous studies on acetylene-linked dendrimers were inspired by Moore's models and applied in areas such as OLEDs[17] and sensors,[18] among others.[19] The excellent performance of **3a** and **3b** made it possible to synthesize CTV-phenylacetylene dendrimers **4k**–**m**. The photophysical and electrochemical properties of these conjugated CTV-phenylacetylene dendrimers have been investigated and are discussed herein.

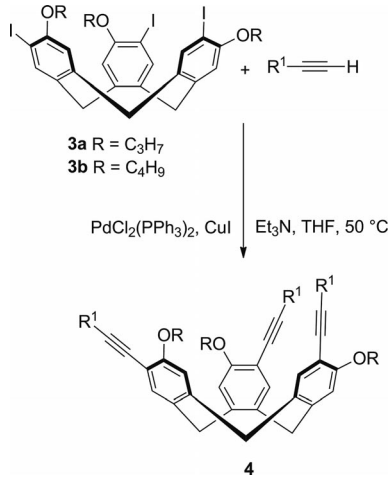
Results and Discussion

Synthesis

As mentioned above, functionalized C_3-cyclotriveratrylenes could be obtained by cyclodehydration of certain 3,4-disubstituted benzyl alcohol derivatives.[20] In this method, acetic acid was usually required as solvent and perchloric acid as catalyst to generate the benzylic cation. However, to our dismay, by using this method we did not obtain the desired product CTV-I_3 starting from 4-iodo-3-methoxybenzyl alcohol. In the synthesis of CTV-Br_3, Cram et al.[9] commented that the bromine in 4-bromo-3-methoxybenzyl alcohol acted as a group that protects the 4-position from alkylation by the benzyl cation. So it seems that 4-iodo-3-methoxybenzyl alcohol could also work by using this protocol. We have found that the methoxy-substituted CTV-I_3 derivative synthesized by Collet and Gosse showed poor solubility in common solvents and could be only solved in dimethyl sulfoxide (DMSO). Isolation of the product from the reaction system by increasing the solubility seems to be the key problem. Collet pointed out that a strongly electron-donating group *para* to the CH_2OH moiety was required. Furthermore, the importance of having a strongly electron-donating substituent *meta* to CH_2OH was also demonstrated.[1a] Thus, the introduction of propyloxy and butoxy groups *meta* to CH_2OH seemed to be a promising approach.

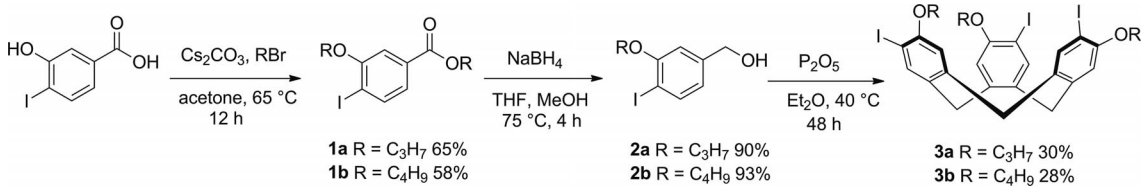
The preparation of **3a** and **3b** is shown in Scheme 1. Starting from 3-hydroxybenzoic acid, iodination took place according to the reported method.[21] Alkylation and esterification of 3-hydroxy-4-iodobenzoic acid were carried out using Cs_2CO_3 as base. Although the reaction only provided a moderate yield, the unreacted material could be acidified with concentrated HCl and recycled. Reduction of **1a** and **1b** to the benzyl alcohol proceeded in a mixture of tetrahydrofuran (THF), $NaBH_4$, and methanol at reflux temperature within 4 h (conversion was determined by TLC analysis). Treatment of **2a** and **2b** with P_2O_5 and Et_2O under reflux gave the cyclotribenzylene compounds **3a** and **3b**, which could be purified by recrystallization from $CHCl_3$/hexane. In contrast to the method developed by Gosse,[13] $NaBH_4$ was used to reduce propyl or butyl ester intermediate without deiodination instead of diisobutylaluminum hydride, which was used at –80 °C. Because of the good solubility of **3a** and **3b**, less solvent was required for elution and recrystallization.

The palladium-catalyzed Sonogashira coupling of **3** with aryl-alkynes is shown in Scheme 2.[22] Sonogashira cross-coupling reaction of **3a** and **3b** with terminal alkynes proceeded smoothly at 50 °C. Heating contributed to the dissolution of **3a** and **3b**. Through the use of $[PdCl_2(PPh_3)_2]$ as a catalyst, CuI as a cocatalyst, and an excess amount of Et_3N as solvent, the reaction afforded moderate to good yields. For aryl-alkynes, the product yield depended on the substitution pattern of the phenyl ring. Electron-rich phenylacetylenes gave better yields (Table 1, entries 1–4) than electron-poor alkynes (Table 1, entries 5–10).[23]



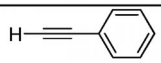
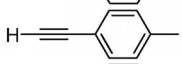
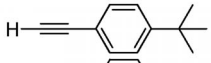
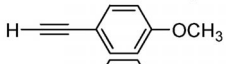
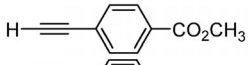
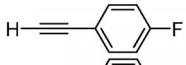
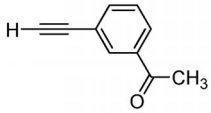
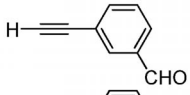
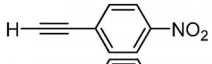
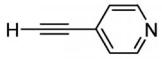
Scheme 2. Palladium-catalyzed Sonogashira coupling of **3** with aryl-alkynes.

Phenylacetylene monodendrons **D-k**, **D-l**, and **D-m** (Figure 1) were synthesized according to the reported convergent method.[24] The higher generation of none *tert*-butyl substituted dendron was not obtained because of its poor solubility. When these monodendrons reacted with **3b**, low yields were obtained. There are two main reasons for this



Scheme 1. Syntheses of C_3-cyclotriveratrylenes iodine derivatives.

Table 1. Palladium-catalyzed Sonogashira coupling of **3** with aryl-alkynes.[a,b]

Entry	Alkyne	(±)-4	% Yield[c]
1		**4a**	84
2		**4b**	77
3		**4c**	82
4		**4d**	80
5		**4e**	54
6		**4f**	78
7		**4g**	71
8		**4h**	53
9		**4i**	40
10		**4j**	70
11	D-k	**4k**	41
12	D-l	**4l**	25
13	D-m	**4m**	28

[a] Reaction conditions for entries 1–8: **3a** (0.365 mmol), aryl-alkynes (1.3 mmol, 1.2 equiv.), CuI (0.016 mmol, 4 mol-%), $[PdCl_2(PPh_3)_2]$ (0.014 mmol, 4 mol-%), Et_3N (10 mL), anhydrous THF (10 mL), 50 °C, 24 h. [b] Entries 9 and 11–13 use **3b** in the reactions, other conditions are same as above. [c] Yield of isolated product.

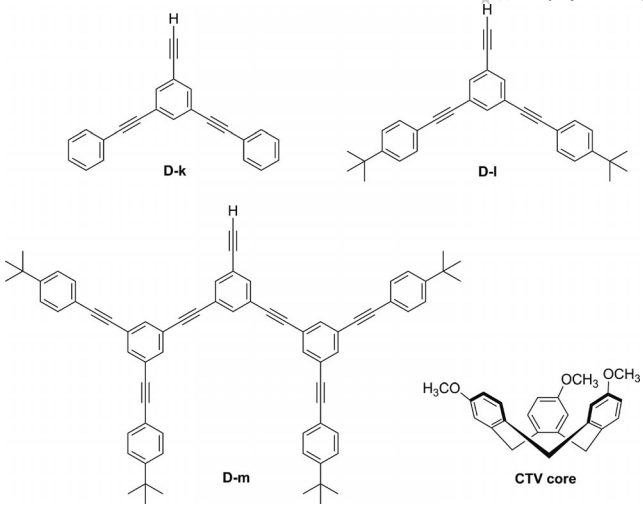


Figure 1. Chemical structures of **D-k**, **D-l**, **D-m** and the CTV core.

result: the diacetylene byproduct of Glaser coupling increases with increasing generation,[16,24] and steric hindrance became more apparent with increasing generation and size. Moreover, generations higher than **D-m** were not synthesized because of the lower fluorescence quantum yields of the product and because Glaser coupling would become more significant.[24]

Visualization and Simulation

The structures of dendrimers **4k**–**m** were modeled by the AM2 method in the Gaussian 09 program;[25] the results are displayed in Figure 2. All three compounds exhibit 'windmill-like' shape. Although **4k**–**m** all bear large dendron

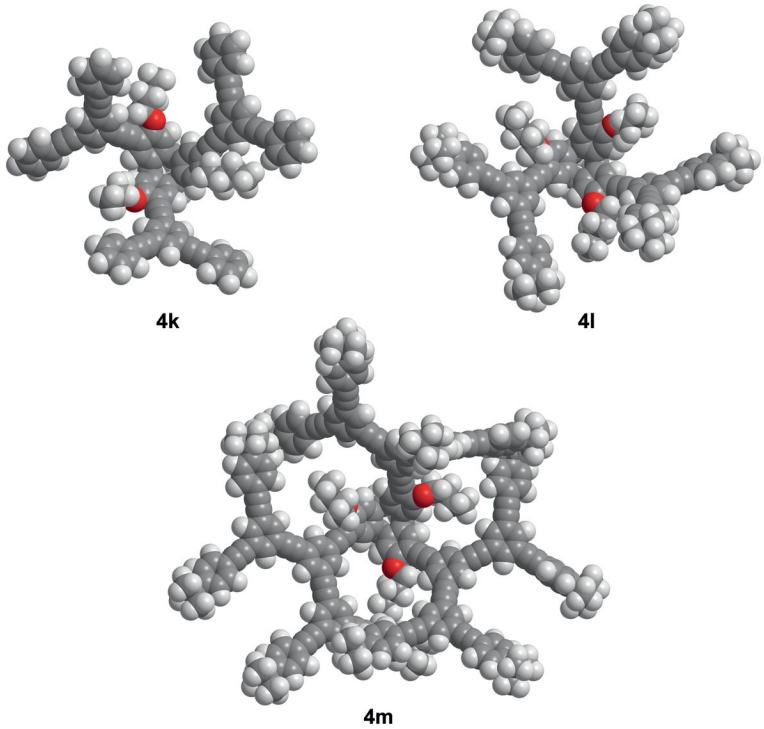


Figure 2. Molecular models of **4k**–**m** optimized by the AM2 method in the Gaussian 09 program.

structures at the upper rims, the cone shape conformation at the center remains unchanged, which can be confirmed by their ^{1}H NMR spectra. In the cone-shaped CTV, the methylene groups in the CTV skeleton show a pair of doublets around δ = 3.6 and 4.7 ppm, whereas in the saddle-shaped CTV only a singlet was found (δ = 3.8 ppm).[26]

The three dendrimers **4k**–**m** can adopt two stereoisomeric forms: *P* and *M* (the dendrimers in Figure 2 are depicted as *M*). Their optimized structures show that the phenylacetylene monodendrons on the upper rim twist in the same direction. It seems that even a large chiral cavity could be realized by introducing the phenylacetylene monodendrons to CTV.

Compared with **4m**, CTV dendrimers **4k** and **4l**, with smaller dendrons at their periphery, show better co-planarity of all the phenyl groups. Compound **4m** possesses more arms at its periphery and the outermost arms are not in the same plane with the phenyl in the CTV core due to steric hindrance. In contrast, the dendrons at the periphery of **4k** and **4l** have good conjugation with the phenyl in the CTV core.

Photophysical Properties

The absorption spectra of dendrimeric CTVs **4k**–**m**, phenylacetylene monodendrons **D-k**, **D-l**, **D-m**, the CTV core, and 1/3 **4k** are shown in Figure 3. The fluorescence spectra of **4k**–**m** are shown in Figure 4. The photophysical data are summarized in Table 2 and Table 3.

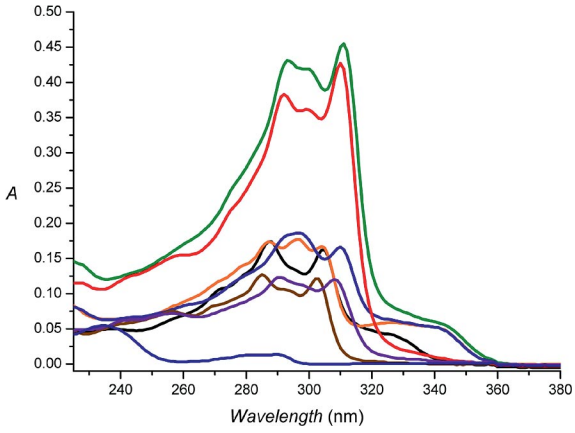


Figure 3. Absorption spectra of **4k**–**m**, **D-k**, **D-l**, **D-m**, 1/3 **4k**, and the CTV core in CH_2Cl_2. (Green) **4m**, (red) **D-m**, (orange) **4k**, (blue) **4l**, (black) 1/3 **4k**, (brown) **D-k**, (purple) **D-l**, (deep-blue) CTV core. The concentrations are normalized to 3.2×10^{-6} L·mol^{-1} for **4k**–**m**, CTV core, and 9.6×10^{-6} L·mol^{-1} for **D-k**, **D-l**, **D-m**, 1/3 **4k**.

From the absorption spectra displayed in Figure 3, it can be seen that the phenylacetylene monodendrons **D-k**, **D-l**, and **D-m** have almost the same absorption bands as their corresponding CTV derivatives. Therefore, the intense absorption bands around 290–310 nm of **4k**–**m** are due to the phenylacetylene dendrons. When the spectra of the CTV core is compared with those of **4k**–**m**, the absorption band

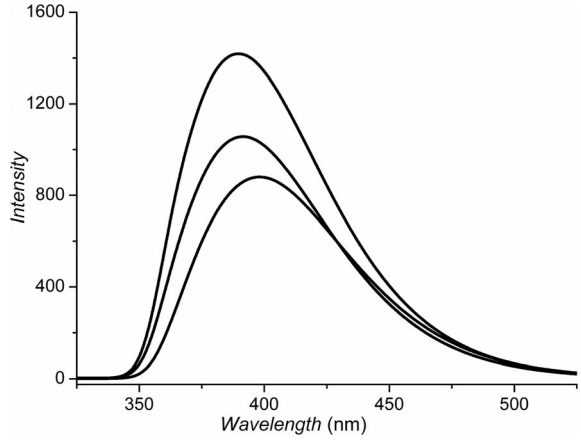


Figure 4. Fluorescence spectra of **4k**–**m** in CH_2Cl_2 excited at 310 nm. From top to bottom: **4l**, **4k**, and **4m**.

Table 2. Photophysical properties.

	λ_{max} [nm][a]	ε [10^5 L·mol^{-1}·cm^{-1}]	ΔE [eV][b]
4k	287, 296, 303, 338	2.70, 2.76, 2.61, 0.83	3.49
4l	297, 310, 338	2.91, 2.58, 0.84	3.49
4m	293, 299, 310, 338	6.70, 6.55, 7.08, 0.92	3.45
D-k	284, 302	0.66, 0.63	–
D-l	290, 307	0.64, 0.63	–
D-m	291, 299, 310	1.99, 1.88, 2.22	–
1/3 **4k**	287, 304, 325	0.91, 0.84, 0.22	3.64

[a] In CH_2Cl_2. [b] Estimated from the absorption edge.

Table 3. Photophysical properties of **4k**–**m**.

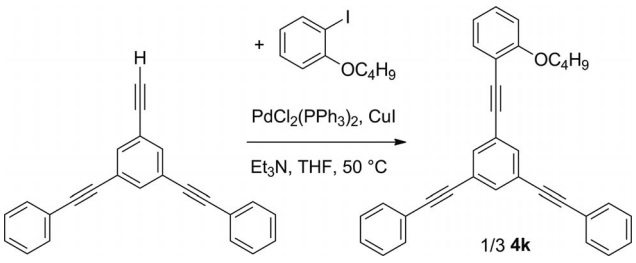
	λ FL_{max} [nm][a]	Φ_{FL}[b]
4k	391	0.64
4l	389	0.78
4m	398	0.48
1/3 **4k**	383	0.34

[a] Excited at 310 nm. [b] Determined with 2-aminopyridine as a standard, when excited at 310 nm.

of the former is probably covered by the absorption bands of phenylacetylene dendrons.

The molar extinction coefficient (ε) of compound **4m** is somewhat larger than that of compounds **4k** and **4l**. This is consistent with phenylacetylene monodendrons **D-k**, **D-l**, and **D-m**, for which the molar extinction coefficient increases with increasing generation. It is interesting that the spectra of **4k**–**m** contain absorption bands around 340 nm; these bands, which are the lowest energy absorption peaks, did not appear in the spectra of **D-k**, **D-l**, **D-m**, or the CTV core. The peaks increase with increasing generations and also shift to red with increasing size, which is typical of conjugated organic molecules.[16] We attribute this absorption band to the conjugation between phenylacetylene monodendron and phenyl in the CTV core. To gain a better understanding of the origins of this absorption band, 1/3 **4k** was synthesized (Scheme 3). As can be observed in its spectrum, the absorption band around 340 nm shifts to 330 nm and the intensity is lower than **4k** at the same concentration. We assumed that the CTV core makes a signifi-

cant contribution to this absorption band, and it may facilitate intramolecular π-interaction of the attached conjugated dendrons.



Scheme 3. Synthesis of 1/3 **4k**.

The band-gaps of **4k**–**m** estimated from the corresponding absorption edge are 3.49, 3.49 and 3.45 eV. The energy gaps decreased with increasing generation because of the extended conjugation. As a result of this unique characteristic, **4k**–**m** could be used as potential host material in OLEDs.

The fluorescence spectra show that the fluorescence maximum does not shift significantly between **4k** and **4l**, but a bathochromic shift of 9 nm between **4l** and **4m** can be seen, which is a characteristic for conjugated systems. The fluorescence intensity decreases with higher generation, which is also a character for dendrimeric systems.[16] The fluorescence quantum yields of **4k**–**m** (determined with 2-aminopyridine as a standard when excited at 310 nm) were 0.64, 0.78, and 0.48, respectively. This result is consistent with the conclusion that the higher generation dendrimers normally have lower quantum yields.[16]

Electrochemical Properties

To gain a better understanding of the character of **4k**–**m** for their application in functional materials, their electrochemical properties were investigated by cyclic voltammetry, which allowed their HOMO and LUMO energy levels to be calculated.[27] The cyclic voltammograms are shown in Figure 5.

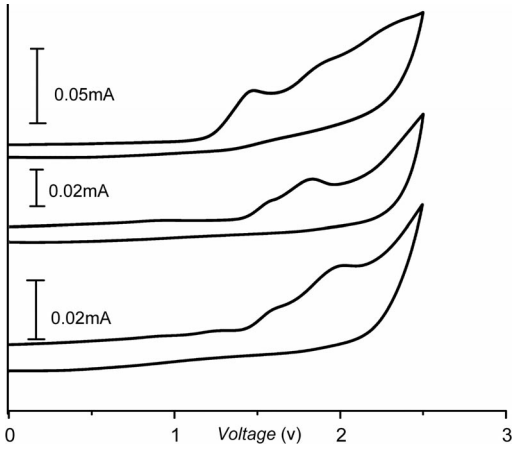


Figure 5. Cyclic voltammograms of (from top to bottom) dendrimers **4m**, **4l**, and **4k** in 0.1 M Bu_4NPF_6/CH_2Cl_2, scan rate 100 mV/s.

The experiments were carried out in 0.1 M Bu_4NPF_6/CH_2Cl_2 at a scan rate of 100 mV/s, and poorly resolved reversible oxidation peaks were observed for **4k**–**m**. The HOMO energy levels, which were estimated on the basis of roughly evaluated onset oxidation potentials (HOMO = E^{ox}_{onset} + 4.7 eV), were calculated to be –6.07, –6.10, and –5.92 eV, respectively. The LUMO energy levels were calculated from the HOMO energy level and energy band gap (E_g), which was determined by the UV/Vis absorption edge (LUMO = HOMO – E_g eV); LUMO energy levels of **4k**–**m** were thus calculated to be –2.58, –2.61, and –2.47 eV, respectively.

Conclusions

This work describes a simple and useful synthetic route, starting with 3-hydroxybenzoic acid, to prepare the key reactants CTV-I_3 **3a** and **3b** for cross-coupling reactions, which showed very good activity when reacted with arylalkynes. A series of functionalized macrocyclic CTV-phenylacetylene derivatives was synthesized. Sonogashira reactions of **3b** with phenylacetylene monodendrons **D-k**, **D-l**, and **D-m** provided the star-like molecules **4k**–**m**. These compounds show good photophysical properties. The fluorescence quantum yield of **4k** and **4l** are as high as 0.64 and 0.78. The band-gaps of **4k**–**m**, estimated from absorption edges, are 3.49, 3.49 and 3.45 eV, respectively, which make these compounds suitable as potential materials for OLEDs. The HOMO energy levels of **4k**–**m**, which were investigated by cyclic voltammetry, are –6.07, –6.10, and –5.92 eV, respectively, whereas the LUMO energy levels are –2.58, –2.61, and –2.47 eV.

The excellent performance of CTV-I_3 derivatives in Sonogashira cross-coupling reactions makes it possible to introduce various functional groups to the CTV upper rim, and the assembly of these new macrocycles is ongoing in our laboratory.

Experimental Section

General: All reactions were carried out under argon atmosphere. Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. [$PdCl_2(PPh_3)_2$] and CuI were purchased from Aldrich. Anhydrous Et_3N was distilled from KOH. Anhydrous THF was distilled from Na. Melting points were recorded with an electrothermal melting point apparatus. IR spectra were recorded with an FTIR-480 spectrometer using KBr discs. The UV/Vis and fluorescence experiments were recorded with Gangdong F-380 and Persee TU-1810, spectrophotometers, respectively. All the electrochemical experiments were carried out with a CHI620D potentiostat. The measurements were carried out in 0.1 M Bu_4NPF_6/CH_2Cl_2 with Ag/AgCl/KCl as the reference electrode and a platinum coil as the counter electrode. Mass spectra were recorded with a Micromass GCT and a Bruker autoflex III instrument. ^1H and ^{13}C NMR spectra were recorded at 25 °C with a Bruker (400 MHz) NMR spectrometer with TMS as internal standard.

[$PdCl_2(PPh_3)_2$]-Catalyzed Sonogashira Coupling Reactions on (±)-2,7,12-Tris(propyloxy)-3,8,13-triiodo-10,15-dihydro-5*H*-tribenzo-

[*a*,*d*,*g*]cyclonoene. General Procedure: Under argon, CuI (0.003 g, 0.016 mmol, 4 mol-%), $[PdCl_2(PPh_3)_2]$ (0.01 g, 0.014 mmol, 4 mol-%), **3a** (0.2 g, 0.365 mmol), and Et_3N (10 mL) were loaded into a Schlenk tube equipped with a Teflon®-coated magnetic stirring bar. After 30 min, the corresponding acetylene (1.3 mmol, 1.2 equiv.) in anhydrous THF (10 mL) was added. The mixture was stirred at 50 °C for 24 h. Upon completion of the reaction, solvents were evaporated and the residue was dissolved in CH_2Cl_2 (50 mL). The organic layer was washed with water and dried with Na_2SO_4. After filtration and concentration, the residue was purified by column chromatography (petroleum ether/CH_2Cl_2) to give the desired product.

(±)-2,7,12-Tris(propyloxy)-3,8,13-tris(phenylethynyl)-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclonoene (4a): Yield 84%; m.p. 268–269 °C. IR (KBr): $\tilde{\nu}$ = 2963, 2934, 2876 (CH_3, CH_2), 2211 (C≡C) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.49 (m, 6 H), 7.43 (s, 3 H), 7.34–7.29 (m, 9 H), 6.87 (s, 3 H), 4.68 (d, J = 13.6 Hz, 3 H), 4.07–3.98 (m, 6 H), 3.60 (d, J = 13.6 Hz, 3 H), 1.88–1.79 (m, 6 H), 1.07 (t, J = 14.8 Hz, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.5, 141.3, 134.5, 131.5, 130.8, 128.2, 127.9, 123.9, 114.1, 111.9, 92.9, 85.9, 70.6, 36.6, 22.6, 10.5 ppm. MS (MALDI-TOF): m/z = 744.2, 767.2 [M + Na^+], 783.2 [M + K^+]. $C_{54}H_{48}O_3$ (744.97): calcd. C 87.09, H 6.34; found C 86.73, H 6.53.

(±)-2,7,12-Tris(propyloxy)-3,8,13-tris[(*p*-tolyl)ethynyl]-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclonoene (4b): Yield 77%; m.p. 247–248 °C. IR (KBr): $\tilde{\nu}$ = 2964, 2927, 2874 (CH_3, CH_2), 2211 (C≡C) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.42 (s, 3 H), 7.39 (d, J = 8.0 Hz, 6 H), 7.12 (d, J = 8.0 Hz, 6 H), 6.86 (s, 3 H), 4.67 (d, J = 13.6 Hz, 3 H), 4.04–3.99 (m, 6 H), 3.59 (d, J = 13.6 Hz, 3 H), 2.35 (s, 9 H), 1.85–1.80 (m, 6 H), 1.06 (t, J = 14.8 Hz, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.4, 141.1, 137.9, 134.4, 131.4, 130.9, 129.0, 120.9, 114.1, 112.1, 93.0, 85.3, 70.6, 36.6, 22.6, 21.5, 10.5 ppm. MS (MALDI-TOF): m/z = 786.3, 809.3 [M + Na^+], 825.3 [M + K^+]. $C_{57}H_{54}O_3$ (787.05): calcd. C 87.01, H 6.78; found C 86.96, H 7.06.

(±)-2,7,12-Tris(propyloxy)-3,8,13-tris{[4-(*tert*-butyl)phenyl]-ethynyl}-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclonoene (4c): Yield 82%; m.p. 263–264 °C. IR (KBr): $\tilde{\nu}$ = 2963, 2872 (CH_3, CH_2), 2211 (C≡C) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.43 (t, J = 8.3 Hz, 9 H), 7.34 (d, J = 8.2 Hz, 6 H), 6.86 (s, 3 H), 4.66 (d, J = 13.6 H, 3 H), 4.06–3.96 (m, 6 H), 3.59 (d, J = 13.6 Hz, 3 H), 1.86–1.78 (m, 6 H), 1.31 (s, 27 H), 1.06 (t, J = 14.8 Hz, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.5, 151.1, 141.1, 134.4, 131.2, 130.9, 125.2, 120.9, 114.2, 112.2, 92.9, 85.3, 70.6, 36.6, 34.7, 31.2, 22.6, 10.5 ppm. MS (MALDI-TOF): m/z = 912.4, 935.4 [M + Na^+], 951.4 [M + K^+]. $C_{66}H_{72}O_3 \cdot 0.5H_2O$: C 85.95, H 7.98; found C 85.72, H 7.81.

(±)-2,7,12-Tris(propyloxy)-3,8,13-tris[(4-methoxyphenyl)ethynyl]-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclonoene (4d): Yield 80%; m.p. 239–240 °C. IR (KBr): $\tilde{\nu}$ = 2963, 2934, 2875 (CH_3, CH_2), 2211 (C≡C), 1248 (C–O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.43 (t, J = 8.6 Hz, 9 H), 6.85 (d, J = 8.0 Hz, 9 H), 4.68 (d, J = 13.6 Hz, 3 H), 4.04–4.00 (m, 6 H), 3.81 (s, 9 H), 3.59 (d, J = 13.6 Hz, 3 H), 1.88–1.79 (m, 6 H), 1.06 (t, J = 14.8 Hz, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4, 158.3, 140.9, 134.3, 132.9, 130.9, 116.1, 114.2, 113.9, 112.2, 92.8, 84.5, 70.6, 55.3, 36.6, 22.6, 10.5 ppm. MS (MALDI-TOF): m/z = 834.3, 857.2 [M + Na^+], 873.2 [M + K^+]. $C_{57}H_{54}O_6 \cdot 0.5H_2O$: C 81.11, H 6.57; found C 81.05, H 6.64.

(±)-2,7,12-Tris(butyloxy)-3,8,13-tris[4-(methoxycarbonyl)phenyl]-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclonoene (4e): Yield 54%; m.p. 231–232 °C. IR (KBr): $\tilde{\nu}$ = 2964, 2876 (CH_3, CH_2), 2211 (C≡C), 1724 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, J = 8.4 Hz, 6 H), 7.54 (d, J = 8.4 Hz, 6 H), 7.45 (s, 3 H), 6.89 (s, 3 H), 4.72 (d, J = 13.6 Hz, 3 H), 4.07–4.02 (m, 6 H), 3.92 (s, 9 H), 3.63 (d, J = 13.6 Hz, 3 H), 1.88–1.83 (m, 6 H), 1.07 (t, J = 14.4 Hz, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 158.7, 141.8, 134.6, 131.3, 130.8, 129.5, 129.2, 128.6, 114.0, 111.4, 92.3, 89.1, 70.6, 52.2, 36.7, 22.6, 10.5 ppm. HRMS (ESI^+): calcd. for $C_{60}H_{54}O_9$ 919.3841; found 919.3882.

(±)-2,7,12-Tris(propyloxy)-3,8,13-tris[(4-fluorophenyl)ethynyl]-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclonoene (4f): Yield 78%; m.p. 240–241 °C. IR (KBr): $\tilde{\nu}$ = 2963, 2877 (CH_3, CH_2), 2212 (C≡C) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.46 (m, 9 H), 7.04–6.99 (m, 6 H), 6.86 (s, 3 H), 4.70 (d, J = 13.6 Hz, 3 H), 4.05–3.99 (m, 6 H), 3.60 (d, J = 13.6 Hz, 3 H), 1.88–1.79 (m, 6 H), 1.06 (t, J = 14.8 Hz, 9 H ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.5, 161.1, 158.5, 141.3, 134.4, 133.3, 133.2, 130.8, 120.0, 119.9, 115.6, 115.4, 114.0, 111.7, 91.8, 85.5, 70.5, 36.6, 22.5, 10.5 ppm. MS (MALDI-TOF): m/z = 798.2, 821.2 [M + Na^+], 837.2 [M + K^+]. $C_{54}H_{45}F_3O_3$ (798.94): calcd. C 81.10, H 5.52; found C 81.44, H 5.54.

(±)-2,7,12-Tris(propyloxy)-3,8,13-tris[(3-acetylphenyl)ethynyl]-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclonoene (4g): Yield 71%; m.p. 167–169 °C. IR (KBr): $\tilde{\nu}$ = 2965, 2935, 2876 (CH_3, CH_2), 2213 (C≡C), 1690 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.09 (s, 3 H), 7.89–7.87 (m, 3 H), 7.69–7.66 (m, 3 H), 7.46–7.41 (m, 6 H), 6.90 (s, 3 H), 4.73 (d, J = 13.6 Hz, 3 H), 4.10–4.02 (m, 6 H), 3.64 (d, J = 13.6 Hz, 3 H), 2.61 (s, 9 H), 1.89–1.83 (m, 6 H), 1.09 (t, J = 14.8 Hz, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.4, 158.7, 141.7, 137.2, 135.7, 134.5, 131.4, 130.8, 128.6, 127.5, 124.5, 114.0, 111.5, 91.9, 87.0, 70.6, 36.6, 26.6, 22.5, 10.5 ppm. MS (MALDI-TOF): m/z = 893.2 [M + Na^+]. $C_{60}H_{54}O_6$ (871.08): calcd. C 82.68, H 6.12; found C 82.98, H 6.14.

(±)-2,7,12-Tris(propyloxy)-3,8,13-tris[(3-formylphenyl)ethynyl]-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclonoene (4h): Yield 53%; m.p. 231–232 °C. IR (KBr): $\tilde{\nu}$ = 2964, 2935, 2876 (CH_3, CH_2), 2211 (C≡C), 1695 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 10.00 (s, 3 H), 7.99 (s, 3 H), 7.82–7.79 (m, 6 H), 7.75–7.72 (m, 6 H), 6.90 (s, 3 H), 4.72 (d, J = 13.6 Hz, 3 H), 4.10–4.01 (m, 6 H), 3.64 (d, J = 13.6 Hz, 3 H), 1.90–1.81 (m, 6 H), 1.08 (t, J = 14.8 Hz, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.6, 158.7, 141.8, 137.0, 136.5, 134.6, 132.7, 130.8, 129.0, 128.7, 125.1, 113.9, 111.4, 91.4, 87.6, 70.5, 36.6, 22.5, 10.5 ppm. MS (MALDI-TOF): m/z = 851.3. $C_{57}H_{48}O_6$ (829.00): calcd. C 82.53, H 5.69; found C 82.60, H 5.62.

(±)-2,7,12-Tris(butyloxy)-3,8,13-tris[(4-nitrophenyl)ethynyl]-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclonoene (4i): Yield 40%; m.p. 310–311 °C. IR (KBr): $\tilde{\nu}$ = 2957, 2935, 2876 (CH_3, CH_2), 2210 (C≡C), 1341 (N=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.20 (d, J=8.8, 6 H), 7.60 (d, J = 8.8 Hz, 6 H), 7.46 (s, 3 H), 6.91(s, 3 H), 4.77 (d, J = 13.6 Hz, 3 H), 4.12–4.08 (m, 6 H), 3.67 (d, J = 13.6 Hz, 3 H), 1.84–1.79 (m, 6 H), 1.58–1.49 (m, 6 H), 0.98 (t, J = 14.8 Hz, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.9, 146.8, 142.4, 134.7, 132.0, 130.8, 130.7, 123.6, 113.8, 110.9, 91.5, 91.4, 68.8, 36.7, 31.1, 19.2, 13.8 ppm. MS (EI^+): m/z = 921. $C_{57}H_{51}N_3O_9$ (922.04): calcd. C 74.07, H 5.44; found C 74.03, H 5.70.

(±)-2,7,12-Tris(butyloxy)-3,8,13-tri(pyridin-4-yl)-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclonoene (4j): Yield 70%; m.p. 266–267 °C. IR (KBr): $\tilde{\nu}$ = 2965, 2934, 2876 (CH_3, CH_2), 2214 (C≡C), 1591, 1405, 1253 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.57 (d, J = 5.6 Hz, 6 H), 7.43 (s, 3 H), 7.33 (d, J = 5.6 Hz, 6 H), 6.85 (s, 3 H), 4.57 (d, J = 13.6 Hz, 3 H), 4.04–3.96 (m, 6 H), 3.54 (d, J = 13.6 Hz, 3 H), 1.84–1.79 (m, 6 H), 1.05 (t, J = 14.8 Hz, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.9, 149.7, 142.3, 134.7, 131.9, 130.7,

125.4, 113.7, 110.7, 90.8, 90.4, 70.4, 36.5, 22.5, 10.5 ppm. HRMS (ESI^+): calcd. for $C_{51}H_{46}O_3N_3$: 748.3534; found 748.3548.

(±)-2,7,12-Tris(butyloxy)-3,8,13-tris{3,5-bis[(phenylethynyl)-phenyl]ethynyl}-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (4k): Yield 41%; m.p. 246–247 °C. IR (KBr): $\tilde{\nu}$ = 2956, 2869 (CH_3, CH_2), 2213 (C≡C) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.62–7.60 (m, 9 H), 7.53–7.51 (m, 12 H), 7.45 (s, 3 H), 7.36–7.34 (m, 18 H), 6.90 (s, 3 H), 4.73 (d, J = 13.6 Hz, 3 H), 4.13–4.09 (m, 6 H), 3.64 (d, J = 13.6 Hz, 3 H), 1.88–1.81 (m, 6 H), 1.63–1.50 (m, 6 H), 1.01 (t, J = 14.8 Hz, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8, 141.6, 134.6, 133.9, 133.7, 131.7, 130.8, 128.5, 128.4, 124.6, 123.9, 122.9, 114.0, 111.5, 91.4, 90.3, 87.9, 87.3, 68.9, 36.7, 31.3, 29.7, 19.3, 13.9 ppm. MS (MALDI-TOF): m/z = 1410.5 [M + Na^+]. $C_{57}H_{54}O_3 \cdot 0.5H_2O$: C 90.29, H 5.70; found C 90.05, H 5.67.

(±)-2,7,12-Tris(butyloxy)-3,8,13-tris(3,5-bis{[(4-*tert*-butylphenyl)-ethynyl]phenyl}ethynyl)-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (4l): Yield 25%; m.p. 275–276 °C. IR (KBr): $\tilde{\nu}$ = 2961, 2869 (CH_3, CH_2), 2213 (C≡C) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.60–7.58 (m, 9 H), 7.45 (d, J = 8.4 Hz, 15 H), 7.37 (d, J = 8.4 Hz, 12 H), 6.89 (s, 3 H), 4.69 (d, J = 13.6 Hz, 3 H), 4.14–4.06 (m, 6 H), 3.62 (d, J = 13.6 Hz, 3 H), 1.87–1.80 (m, 6 H), 1.63–1.53 (m, 6 H), 1.32 (s, 54 H), 1.02 (t, J = 14.8 Hz, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8, 151.8, 141.6, 134.6, 133.8, 133.6, 131.4, 130.8, 125.4, 124.6, 124.1, 119.9, 113.9, 111.6, 91.5, 90.5, 87.4, 87.2, 68.9, 36.6, 34.8, 31.3, 31.2, 19.4, 14.0 ppm. MS (MALDI-TOF): m/z = 1746.5 [M + Na^+]. $C_{129}H_{126}O_3$ (1724.41): calcd. C 89.99, H 7.13; found C 89.59, H 7.22.

(±)-2,7,12-Tris(butyloxy)-3,8,13-tris{[3,5-bis({3,5-bis[(4-*tert*-butylphenyl)ethynyl]phenyl}ethynyl)phenyl]ethynyl}-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (4m): Yield 28%; m.p. 217–218 °C. IR (KBr): $\tilde{\nu}$ = 2961, 2869 (CH_3, CH_2), 2213 (C≡C) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.64–7.61 (m,26 H), 7.46 (d, J = 8 Hz, 26 H), 7.36 (d, J = 8 Hz, 26 H), 6.93 (s, 3 H), 4.75 (d, J = 13.6 Hz, 3 H), 4.15–4.13 (m, 6 H), 3.67 (d, J = 13.6 Hz, 3 H), 1.90–1.83 (m, 6 H), 1.66–1.60 (m, 6 H), 1.31 (s, 108 H), 1.04 (t, J = 14.8 Hz, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8, 151.9, 141.8, 134.7, 134.3, 133.9, 131.5, 130.8, 125.4, 124.8, 124.3, 123.6, 123.5, 119.8, 114.0, 111.5, 91.3, 90.8, 89.0, 88.8, 87.6, 87.2, 68.9, 36.7, 34.8, 31.2, 31.1, 19.4, 14.0 ppm. MS (MALDI-TOF): m/z = 3284.3 [M + Na^+]. $C_{249}H_{222}O_3 \cdot CH_2Cl_2$: C 89.70, H 6.74; found C 89.49, H 6.68.

{5-[(2-Butoxyphenyl)ethynyl]-1,3-phenylene}bis(ethyne-2,1-diyl)-dibenzene (1/3 D-k): Yield 82%. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.51 (s, 3 H), 7.49–7.37 (m, 4 H), 7.37–7.27 (m, 7 H), 6.94–6.89 (m, 2 H), 4.09–4.04 (t, J = 12.4 Hz, 2 H), 1.91–1.84 (m, 2 H), 1.66–1.53 (m, 2 H), 1.04 (t, J = 14.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 134.0, 133.7, 133.3, 131.7, 130.0, 128.5, 128.4, 124.6, 123.9, 122.9, 120.3, 112.5, 112.1, 91.7, 90.3, 87.9, 87.3, 68.5, 31.3, 19.3, 13.9 ppm. HRMS (EI^+): calcd. for $C_{34}H_{26}O$ [M + H^+] 450.1984; found 450.1988.

Synthesis of 1a and 1b. General Procedure: A 500 mL two-neck round-bottomed flask was charged with 3-hydroxy-4-iodobenzoic acid (8 g, 30.3 mmol), Cs_2CO_3 (40 g, 2 equiv.), RBr (C_3H_7Br, 9 g, 1.2 equiv. C_4H_9Br, 10 g, 1.2 equiv.) and acetone (200 mL). The mixture was heated a further 12 h at reflux, then the inorganic solids were filtered off, and the solvent was evaporated. The residue was extracted several times with water and dichloromethane. The combined organic layer was dried (Na_2SO_4) and the aqueous layer was combined and acidified with concd. HCl. The unreacted material that remained in water could be recycled. After filtration, dichloromethane was evaporated to yield **1** as a colorless oil, which was pure enough for the next step.

Compound 1a: Yield 6.85 g (65%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, J = 8.0 Hz, 1 H), 7.42 (d, J = 8.0 Hz, 1 H), 7.36–7.34 (m, 1 H), 4.27 (t, J = 13.2 Hz, 2 H), 4.05 (t, J = 12.4 Hz, 2 H), 1.91–1.74 (m, 4 H), 1.10 (t, J = 14.8 Hz, 3 H), 1.02 (t, J = 14.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.2, 157.7, 139.3, 131.9, 123.0, 112.2, 93.1, 70.9, 66.8, 22.4, 22.1, 10.7, 10.4 ppm. HRMS (EI^+): calcd. for $C_{13}H_{17}O_3I$ [M + H^+] 348.0222; found 348.0227.

Compound 1b: Yield 6.67 g (58%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, J = 8.0 Hz, 1 H), 7.41 (s, 1 H), 7.35 (d, J = 8.0 Hz, 1 H), 4.31 (t, J = 13.2 Hz, 2 H), 4.08 (t, J = 12.8 Hz, 2 H), 1.86–1.80 (m, 2 H), 1.76–1.71 (m, 2 H), 1.59–1.43 (m, 4 H), 1.02–0.96 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.2, 157.7, 139.3, 131.9, 123.0, 112.2, 93.1, 69.1, 65.1, 31.0, 30.7, 19.3, 19.2, 13.8, 13.7 ppm. HRMS (EI^+): calcd. for $C_{15}H_{21}O_3I$ [M + H^+] 376.0535; found 376.0540.

Synthesis of 2a and 2b. General Procedure: Compound **1a** (5 g, 14.4 mmol) and $NaBH_4$ (10 g, 263 mmol) were dissolved in anhydrous THF (150 mL) in a 500 mL two-neck round-bottomed flask. After heating to reflux for 30 min, methanol (8 mL) was added over 30 min. The mixture was heated for 4 h at reflux and, after cooling to room temperature, the reaction mixture was quenched by the addition of saturated aqueous NH_4Cl. The aqueous solution was extracted with ethyl acetate and dried (Na_2SO_4). The concentrated residue was purified by column chromatography (petroleum ether/ethyl acetate) to give the product as a colorless oil.

Compound 2a: Yield 3.77 g (90%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, J = 8.0 Hz, 1 H), 6.83 (s, 1 H), 6.68–6.66 (m, 1 H), 4.64 (d, J = 4.8 Hz, 2 H), 3.98 (t, J = 12.8 Hz,2 H), 1.90–1.81 (m, 2 H), 1.09 (t, J = 15.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.8, 142.8, 139.3, 120.5, 110.5, 85.3, 70.7, 64.8, 22.5, 10.7 ppm. HRMS (EI^+): calcd. for $C_{10}H_{13}O_2I$ [M + H^+] 291.9960; found 291.9964.

Compound 2b: Yield 3.78 g (93%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, J = 11.2 Hz, 1 H), 6.81 (d, J = 11.2 Hz, 1 H), 6.66–6.63 (m, 1 H), 4.60 (s, 2 H), 4.00 (t, J = 11.8 Hz,2 H), 1.83–1.79 (m, 2 H), 1.58–1.52 (m, 2 H), 0.99 (t, J = 14.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.9, 142.8, 139.3, 120.5, 110.5, 85.3, 68.9, 64.7, 31.2, 19.3, 13.8 ppm. HRMS (EI^+): calcd. for $C_{11}H_{15}O_2I$ [M + H^+] 306.0117; found 306.0120.

Synthesis of 3a and 3b. General Procedure: To a rapidly stirred mixture of P_2O_5 (16 g, 113 mmol) suspended in anhydrous ether (200 mL) was slowly added **2a** (8 g, 27.4 mmol). The mixture was warmed to reflux temperature and stirred for 2 d. The ether was evaporated and the residue was triturated with $CHCl_3$. A fine white product was formed in this $CHCl_3$ solution on cooling to 0 °C overnight. The product was filtered and washed with water, then dried under vacuum.

Compound 3a: Yield 2.25 g (30%); m.p. 306–307 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.69 (s, 3 H), 6.70 (s, 3 H), 4.61 (d, J = 13.6 Hz, 3 H), 4.03–3.91 (m, 6 H), 3.54 (d, J = 13.6 Hz, 3 H), 1.84–1.79 (m, 6 H), 1.06 (t, J = 14.8 Hz, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.6, 140.7, 140.3, 132.8, 113.4, 84.9, 70.9, 36.0, 22.4, 10.7 ppm. MS (MALDI-TOF): m/z = 821.8, 844.8 [M + Na^+], 860.2 [M + K^+]. $C_{30}H_{33}I_3O_3$ (822.30): calcd. C 3.82, H 4.05; found C 43.91, H 4.08.

Compound 3b: Yield 2.11 g (28%); m.p. 263–264 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.68 (s, 3 H), 6.69 (s, 3 H), 4.55 (d, J = 13.6 Hz, 3 H), 4.06–3.93 (m, 6 H), 3.49 (d, J = 13.6 Hz, 3 H), 1.80–1.74 (m, 6 H), 1.56–1.47 (m, 6 H), 0.97 (t, J = 14.8 Hz, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.6, 140.5, 140.3, 132.8, 113.4,

84.9, 69.1, 36.0, 31.0, 19.3, 13.8 ppm. MS (MALDI-TOF): *m/z* = 886.8 [M + Na^+]. $C_{33}H_{39}I_3O_3$ (864.38): calcd. C 45.85, H 4.55; found C 45.64, H 4.59.

Supporting Information (see footnote on the first page of this article): ^1H and ^{13}C NMR spectra of all the products, high-resolution mass spectra of **1a**, **1b**, **2a**, **2b**, 1/3 **4k**, **4e**, and **4j**.

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[1] a) A. Collet, *Tetrahedron* **1987**, *43*, 5725; b) T. Brotin, J.-P. Dutasta, *Chem. Rev.* **2009**, *109*, 88; c) M. J. Hardie, *Chem. Soc. Rev.* **2010**, *39*, 516.

[2] a) B. Bredenkötter, S. Henne, D. Volkmer, *Chem. Eur. J.* **2007**, *13*, 9931; b) D. S. Bohle, D. J. Stasko, *Inorg. Chem.* **2000**, *39*, 5768; c) Y. M. Dong, D. M. Chen, *Sci. China Ser. B* **2009**, *7*, 986; d) M. J. Hardie, R. Ahmad, *Supramol. Chem.* **2006**, *18*, 29.

[3] a) A. Secchi, A. Arduini, F. Calzavacca, D. Demuru, A. Pochini, *J. Org. Chem.* **2004**, *69*, 1386; b) M. J. Hardie, R. M. Mills, C. J. Sumby, *Org. Biomol. Chem.* **2004**, *2*, 2958; c) D. J. Cram, *J. Chem. Soc., Chem. Commun.* **1988**, 407; d) M. J. Hardie, R. Ahmad, C. J. Sumby, *New J. Chem.* **2005**, *29*, 1231; e) L. Wang, G.-T. Wang, X. Zhao, X.-K. Jiang, Z.-T. Li, *J. Org. Chem.* **2011**, *76*, 3531.

[4] For some examples, see: a) E. Huerta, J. de Mendoza, G. A. Metselaar, *Angew. Chem.* **2007**, *119*, 206; *Angew. Chem. Int. Ed.* **2007**, *46*, 202; b) J. L. Atwood, J. W. Steed, P. C. Junk, *J. Am. Chem. Soc.* **1994**, *116*, 10346; c) J. L. Atwood, M. J. Barnes, M. G. Gardiner, C. L. Raston, *Chem. Commun.* **1996**, 1449; d) M. J. Hardie, C. L. Raston, *Chem. Commun.* **2001**, 905; e) D. V. Konarev, R. N. Lyubovskaya, G. Saito, *Chem. Commun.* **2002**, 2548; f) J. de Mendoza, E. Huerta, E. Cequier, *Chem. Commun.* **2007**, 5016; g) S.-H. Chiu, M.-J. Li, C.-C. Lai, Y.-H. Liu, *Chem. Commun.* **2009**, 5814; h) A. Collet, T. Brotin, A. Lesage, L. Emsley, *J. Am. Chem. Soc.* **2000**, *122*, 1171; i) J. de Mendoza, E. Huerta, H. Isla, E. M. Pérez, C. Bo, *J. Am. Chem. Soc.* **2010**, *132*, 5351; j) J. L. Atwood, A. M. Bond, W. J. Miao, C. L. Raston, T. J. Ness, M. J. Barnes, *J. Phys. Chem. B* **2001**, *105*, 1687; k) J. L. Atwood, K. T. Holman, M. Staffilani, G. Bonvicini, J. W. Steed, M. R. J. Elsegood, *Organometallics* **1998**, *17*, 1732; l) M. R. Caira, A. Jacobs, L. R. Nassimbeni, *Supramol. Chem.* **2004**, *16*, 337; m) I. V. Lijanova, J. F. Maturanoa, J. G. D. Cháveza, K. E. S. Montes, S. H. Ortegaa, T. Klimovab, M. M-García, *Supramol. Chem.* **2009**, *1*, 24.

[5] For some examples, see: a) Y.-Y. Shi, J.-L. Sun, Z.-T. Huang, Q.-Y. Zheng, *Cryst. Growth Des.* **2010**, *10*, 314; b) B. F. Abrahams, R. Robson, *Angew. Chem.* **2010**, *122*, 2958; *Angew. Chem. Int. Ed.* **2010**, *49*, 2896; c) M. J. Hardie, C. J. Sumby, *Angew. Chem.* **2005**, *117*, 6553; *Angew. Chem. Int. Ed.* **2005**, *44*, 6395; d) M. J. Hardie, T. K. Ronson, J. Fisher, L. P. Harding, *Angew. Chem.* **2007**, *119*, 9244; *Angew. Chem. Int. Ed.* **2007**, *46*, 9086; e) M. J. Hardie, T. K. Ronson, J. Fisher, L. P. Harding, P. J. Rizkallah, J. E. Warren, *Nat. Chem.* **2009**, *1*, 212; f) M. J. Hardie, A. Westcott, J. Fisher, L. P. Harding, P. Rizkallah, *J. Am. Chem. Soc.* **2008**, *130*, 2950; g) M. J. Hardie, T. K. Ronson, H. Nowell, A. Westcott, *Chem. Commun.* **2011**, *47*, 176; h) M. J. Hardie, C. J. Sumby, J. Fisher, T. J. Prior, *Chem. Eur. J.* **2006**, *12*, 2945; i) M. J. Hardie, C. Carruthers, T. K. Ronson, C. J. Sumby, A. Westcott, L. P. Harding, T. J. Prior, P. Rizkallah, *Chem. Eur. J.* **2008**, *14*, 10286; j) M. J. Hardie, T. K. Ronson, *CrystEngComm* **2008**, *10*, 1731; k) M. J. Hardie, T. K. Ronson, C. Carruthers, J. Fisher, T. Brotin, L. P. Harding, *Inorg. Chem.* **2010**, *49*, 675.

[6] a) M. J. Hardie, R. Ahmad, A. Franken, J. D. Kennedy, *Chem. Eur. J.* **2004**, *10*, 2190; b) S. Zhang, L. Echegoyen, *J. Am. Chem. Soc.* **2005**, *127*, 2006; c) A. Collet, C. Carcia, *Bull. Soc. Chim. Fr.* **1993**, *130*, 93.

[7] For some examples, see: a) C. Hilty, T. J. Lowery, D. E. Wemmer, A. Pines, *Angew. Chem.* **2006**, *118*, 76; *Angew. Chem. Int. Ed.* **2006**, *45*, 70; b) A. Schlundt, W. Kilian, M. Beyermann, J. Sticht, C. Freund, *Angew. Chem.* **2009**, *121*, 4206; *Angew. Chem. Int. Ed.* **2009**, *48*, 4142; c) A. Collet, T. Brotin, T. Devic, A. Lesage, L. Emsley, *Chem. Eur. J.* **2001**, *7*, 1561; d) P. Berthault, G. Huber, T. Brotin, L. Dubois, H. Desvaux, J.-P. Dutasta, *J. Am. Chem. Soc.* **2006**, *128*, 6239; e) A. Pines, M. M. Spence, E. J. Ruiz, S. M. Rubin, T. J. Lowery, N. Winssinger, P. G. Schultz, D. E. Wemmer, *J. Am. Chem. Soc.* **2004**, *126*, 15287; f) Q. Wei, G. K. Seward, P. A. Hill, B. Patton, I. E. Dimitrov, N. N. Kuzma, I. J. Dmochowski, *J. Am. Chem. Soc.* **2006**, *128*, 13274; g) A. Pines, L. Schröder, T. J. Lowery, C. Hilty, D. E. Wemmer, *Science* **2006**, *314*, 446.

[8] J.-T. Yu, J.-L. Sun, Z.-T. Huang, Q.-Y. Zheng, *CrystEngComm* **2012**, *14*, 112.

[9] D. J. Cram, M. E. Tanner, S. J. Keipert, C. B. Knobler, *J. Am. Chem. Soc.* **1991**, *113*, 8909.

[10] J.-T. Yu, Z.-T. Huang, Q.-Y. Zheng, *Org. Biomol. Chem.* **2012**, *10*, 1359.

[11] R. Chinchilla, C. Najera, *Chem. Rev.* **2007**, *107*, 874.

[12] A. Collet, C. Carcia, *Bull. Soc. Chim. Fr.* **1995**, *132*, 52.

[13] L. Peyrard, S. Chierici, S. Pinet, P. Batat, G. Jonusauskas, N. Pinaud, P. Meyrande, I. Gosse, *Org. Biomol. Chem.* **2011**, *9*, 8489–8494.

[14] J. F. Eckert, D. Byrne, J. F. Nicoud, L. Oswald, J. F. Nierengarten, M. Numata, A. Ikeda, S. Shinkai, N. Armaroli, *New J. Chem.* **2000**, *24*, 749.

[15] a) M. Peterca, V. Percec, M. R. Imam, P. Leowanawat, K. Morimitsu, P. A. Heiney, *J. Am. Chem. Soc.* **2008**, *130*, 14840; b) V. Percec, M. R. Imam, M. Peterca, D. A. Wilson, P. A. Heiney, *J. Am. Chem. Soc.* **2009**, *131*, 1294.

[16] a) C. Devadoss, P. Bharathi, J. S. Moore, *J. Am. Chem. Soc.* **1996**, *118*, 9635; b) Z. F. Xu, M. Kahr, K. L. Walker, C. L. Wilkins, J. S. Moore, *J. Am. Chem. Soc.* **1994**, *116*, 4537; c) P. Bharathi, U. Patel, T. Kawaguchi, D. J. Pesak, J. S. Moore, *Macromolecules* **1995**, *28*, 5955.

[17] S. W. Cha, S. H. Choi, K. Kim, J. I. Jin, *J. Mater. Chem.* **2003**, *13*, 1900.

[18] a) V. J. Pugh, Q. S. Hu, *Angew. Chem.* **2000**, *112*, 3784; *Angew. Chem. Int. Ed.* **2000**, *39*, 3638; b) V. J. Pugh, Q. S. Hu, *J. Org. Chem.* **2001**, *66*, 6136.

[19] a) T. Itoh, T. Maemura, Y. Ohtsuka, Y. Ikari, H. Wildt, K. Hirai, H. Tomioka, *Eur. J. Org. Chem.* **2004**, 2991; b) L. X. Liao, F. Stellacci, D. V. McGrath, *J. Am. Chem. Soc.* **2004**, *126*, 2181; c) S. C. Zimmerman, Y. Wang, P. Bharathi, J. S. Moore, *J. Am. Chem. Soc.* **1998**, *120*, 2172; d) J. N. Clifford, A. Gegout, S. Zhang, R. P. De Freitas, M. Urbani, M. Holler, P. Ceroni, J.-F. Nierengarten, N. Armaroli, *Eur. J. Org. Chem.* **2007**, 5899; e) Y. Yamaguchi, T. Ochi, S. Miyamura, T. Tanaka, S. Kobayashi, T. Wakamiya, Y. Matsubara, Z. Yoshida, *J. Am. Chem. Soc.* **2006**, *128*, 4504; f) J. G. Rodriguez, J. Esquivias, A. Lafuente, C. Diaz, *J. Org. Chem.* **2003**, *68*, 8120; g) Z. Zhao, J. H. Li, X. Chen, X. Wang, P. Lu, Y. Yang, *J. Org. Chem.* **2009**, *74*, 383; h) T. S. Ahn, A. L. Thompson, P. Bharathi, A. Muller, C. J. Bardeen, *J. Phys. Chem. B* **2006**, *110*, 19810.

[20] a) A. Collet, *Tetrahedron* **1987**, *43*, 5725; b) C. Garcia, A. Collet, *Supramol. Chem.* **1992**, *1*, 31.

[21] G. S. Cockerill, P. C. Levett, D. A. Whiting, *J. Chem. Soc. Perkin Trans. 1* **1995**, *9*, 1103.

[22] L. Peyrard, M.-L. Dumartin, S. Chierici, S. Pinet, G. Jonusauskas, P. Meyrand, I. Gosse, *J. Org. Chem.* **2012**, *77*, 7023–7027. After submitting this paper, we found that Gosse group published the first Sonogashira cross-coupling reaction by using the methoxy-substituted CTV-I_3 derivative almost at the

same time. In their work, only two examples (ethynylbenzene and trimethyl-silylacetylene) were given.
[23] a) A. Souffrin, C. Croix, M.-C. Viaud-Massuard, *Eur. J. Org. Chem.* **2012**, 2499; b) F. Yang, Y. Wu, *Eur. J. Org. Chem.* **2007**, 3476–3479; c) E. Negishi, L. Anastasia, *Chem. Rev.* **2003**, *103*, 1979–2017.
[24] C. Y. Wang, H. B. Zhong, S. S. Li, W. F. Shu, Y. J. Shen, *Chin. J. Chem.* **2010**, *28*, 699.
[25] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09*, rev. A.02, Gaussian, Inc., Wallingford CT, **2009**.
[26] H. Zimmermann, P. Tolstoy, R. Poupko, Z. Luz, *J. Phys. Chem. B* **2004**, *108*, 18772–18778.
[27] Y. Yang, Z.-J. Zhao, J.-H. Li, X.-P. Chen, X.-M. Wang, *J. Org. Chem.* **2009**, *74*, 383.

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