



Expanding the *carbo*-benzene chemical space for electron-accepting ability:

trifluorotolyl / tertiobutyl substitution balance⁺

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⁺This paper is dedicated to Prof. François Diederich on the occasion of his retirement.



Spatial remote trifluoromethylation induce an effective expansion of the carbo-benzene chemical space.

Abstract. With the view to altering the lipophilicity and electron accepting ability of the well-proven tetraphenyl-*carbo*-benzene scaffold, peripheral fluorination of the C₁₈ ring through aromatic linkers was envisaged from the C₁₈Ph₆ and $o^{-t}Bu_2C_{18}Ph_4$ references, by replacement of two Ph substituents with two *p*-CF₃-C₆H₄ counterparts (^FTol). The synthesis relied on a [8+10] macrocyclization involving a common bis(trifluorotolyl)-tetraynedione, followed by reductive aromatization of the resulting [6]pericyclynediols. While *p*-^FTol₂C₁₈Ph₄ proved to be hardly tractable due to extremely low solubility, *p*-^FTol₂-*o*-^tBu₂C₁₈Ph₂ could be extensively studied by X-ray crystallography, NMR and UV-vis spectroscopy, voltammetry, STM imaging of monolayers, and AFM imaging of binary films with P₃HT or PC₇₂BM fabricated by spin-coating for organic photovoltaic cells and *J*-*V* curve measurement thereof. The electronic and polarity properties are correlated with moderate but consistent electron-withdrawing effects of the CF₃ groups, in agreement with the DFT-calculated frontier orbitals and multipole moments. The results provide guidelines for optimization of fluorinated *carbo*-benzene targets.

Keywords: carbo-benzene • electron accepting ability • crystal and surface packing • tertiobutyl substitution effect • trifluoromethyl substitution effect

Introduction

Tuning physical or biological properties of organic compounds by formal C-H fluorination or trifluoromethylation of their molecular structure is a current approach in material, pharmaceutical or agrochemical sciences.^[1] Basically, the high electronegativity, ionization potential, small size and low polarizability of dispersive F atoms,^[2] allow fluorination to significantly affect lipophilicity, solubility, viscosity, density, surface tension, boiling point and reactivity, with minor alteration of the global molecular shape and size. In particular, general processability issues can thus be addressed by fluorination of aliphatic or aromatic hydrocarbon moieties of parent carbon-rich molecules or polymers. In the case of carbo-benzene derivatives, characterized by a rigid 8 Å-wide C_{18} aromatic core, ^[4-9] low solubility is a that only recurrent issue can not prevent accurate spectroscopic/electrochemical characterization, but also hamper uses for applications requiring concentrated solutions.^[10-11] This limitation being apriori more pregnant for aryl-substituted representatives, enhancement of solubility was first recently achieved by anchoring branched tert-butyl groups,^[12] or linear alkyl chains $C_n H_{2n+1}$ (n \ge 4) to the C_{18} core.^[13-14] While remote fluorination of octyl chains in the latter series (from C_8H_{17} to $C_2H_4C_6F_{13}$) was observed to have negligible effects on both the solubility and melting-decomposition point, ^[14] direct anchoring of CF_3 groups to the C_{18} macrocycle of hexaoxy[6]pericyclynes^[15-18] was shown to prevent reductive aromatization to the corresponding *carbo*-benzene.^[19-21] Attachment of fluorinated groups through aryl linkers was therefore considered as an alternative by resorting to trifluorotolyl substituents.

Fluorinated substituents are also relevant for their anticipated electronwithdrawing effects on the *carbo*-benzene ring. The low reduction potential of *carbo*-benzenes indeed makes them potential candidates as electron acceptors for application in organic photovoltaics.^[11] With the view to tuning both the solubility and reduction potential of the reference hydrocarbon *carbo*-benzenes **1a** and **1b** (Figure 1), fluorinated homologues were thus devised: the quadrupolar *p*-bis-trifluorotolyl-tetraphenyl-*carbo*benzene **2a**, and the dipolar *p*-bistrifluorotolyl-diphenyl-ditertiobutyl*carbo*-benzenes **2b**. Their synthesis and properties are hereafter described.



Figure 1. Hydrocarbon *carbo*-benzene references 1a and 1b, and retrosynthetic approach to the fluorinated derivatives 2a and 2b.

Following a proven strategy,^[5] the targets **2a** and **2b** were envisaged by reductive aromatization of the corresponding hexaoxy[6]pericyclynediol precursors **3a** and **3b**, themselves targeted by [8+10] macrocyclization reactions between the common decatriyndione **5** and the two known octatriynes **4a** and **4b**, respectively.^[12,17,18] A *meso/dl* mixture of the diketone **5** was prepared in two steps from a *meso/dl* mixture of the diphenylated triyne **4a** (Scheme 1): double deprotonation of **4a** with ⁿBuLi followed by addition to two equivalents of trifluoromethylbenzaldehyde gave the triyndiol **6**, which, upon treatment with MnO₂, lead to **5** with 56 % overall yield.



Scheme 1. Preparation of the diketone 5, common precursor for the synthesis of the *carbo*-benzenes 2a and 2b (Figure 1).

[8+10] Macrocyclization between the C₈ dinucleophile **4a** or **4b** and the C₁₀ dielectrophile **5** was performed in diluted THF solutions in the presence of LiHMDS (Scheme 2). The [6]pericyclynediols **3a** and **3b** could not be isolated in the pure state but were partially purified by silica gel chromatography (see Supporting Information) before treatment with SnCl₂ and HCl•Et₂O in DCM.



Scheme 2. [8+10] macrocyclization and reductive aromatization reactions affording the bis(trifluorototyl)-*carbo*-benzenes **2a** and **2b** (nd = "not determined").

Contrary to the expected solubilizing effect of the trifluorotolyl substituents, the hexaaryl-*carbo*-benzene **2a** happens to be very poorly soluble in organic solvents, even less than its hexaphenyl parent **1a**,^[11] thus preventing full characterization. Nevertheless, residual solubility in THF allowed confirmation of the structure **2a** by ³H and ³⁹F NMR spectroscopy, UV-vis absorption ($\lambda_{max} = 478$ nm in THF, vs 472 nm for **1a** in CHCl₃) and mass spectrometry (m/z = 814.209). The lower solubility of **2a** vs **1a** can be correlated with a twenty-time increase in the calculated in-plane quadrupole anisotropy (see Supporting Information).^[31,22-24] In correlation with the dispersive effects of the tertiobutyl groups, **2b** was found more soluble, allowing full characterization by ³H, ³³C, ³⁹F NMR, mass spectrometry, UV-visible spectroscopy and X-ray crystallography.

The ³H NMR spectrum of **2b** in CDCl₃ exhibit classical features of arylsubstituted *carbo*-benzenes, with a magnetic deshielding of the *ortho*-³H nuclei of the phenyl and trifluorotolyl substituents at 9.51 and 9.64 ppm induced by a strong diatropic ring current around the C_{18} ring. The ^tBu ³H nuclei also resonate at low field (2.53 ppm), as previously reported for other tertiobutyl-substituted *carbo*-benzenes.^[12]

Single crystals of **2b**, deposited from a dichloromethane solution upon slow evaporation at room temperature, were analyzed by X-ray diffraction (Figure 2 and Table 1).^[25,26] In the crystal state, the C₁₈ macrocycle of **2b** is almost planar, with a maximum deviation from the mean plane of $\Delta = 0.130$ Å, i.e. lower than the deviation previously measured for **1b** ($\Delta = 0.244$ Å).^[12] The C₁₈ ring exhibits an almost regular hexagonal shape, with classical bond length and bond angle values ($spC-spC = 1.224 \pm 0.009$ Å, $spC-sp^2C \approx 1.383 \pm 0.013$ Å, $\alpha = 118.8 \pm 0.7$ °). The angles θ between the C₁₈ ring mean plane and the aryl C₆ ring planes vary from 8.1 to 19.8°, thus significantly lower than in **1b** (12.9 to 30.8°).^[12]

In the crystal, the molecules of **2b** pack in columns, the axes of which are not perpendicular to the mean planes of the constituting macrocycles, but slanted by an angle of 57.3° vs the normal to these mean planes. The distance between two successive C₁₈ mean planes is of 3.39 Å, close to the shortest C...C distance between two carbon atoms of two neighboring macrocycles (3.37 Å). These short distances evidence π - π stacking interactions between partially overlapped C₁₈ macrocycles (over *ca* 13% of their parallel hexagonal areas, see Figure 2), and can be compared to those previously reported for the *p*-bis(tetradecyl)-tetraphenyl-*carbo*-benzene (inter-plane distance of 3.21 Å for a shortest internuclear distance of 3.36 Å).^[14] In the crystal of **2b** it can also be noted that the distance between one H atom of a ^fBu group pointing towards the center of the neighboring macrocycle (1.88 Å) is much larger than in the crystal of **1b** (1.20 Å).^[12]

The melting points of **2a** (170°C) and **2b** (161°C) are significantly smaller and sharper (liquid **2a** and **2b** are clearly seen) than the melting-decomposition temperatures of **1a** (221/250°C)^[5,7,11] and **1b** (280°C),^[12] in agreement with the intermolecular lubricating effect of the CF3 groups.

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Figure 2. Molecular view of the X-ray crystal structure of **2b** with hydrogen atoms omitted for clarity (*top*) and π - π stacking overlap between nearest C₁₈ rings over *ca* 13 % of their respective encompassed areas (*bottom*). From data in CCDC 1895113.

Table 1. Selected crystallographic data for 2b and its tetraphenylated analogue 1b.

Species	2b	1b ^ª
Space group	P21	P21/n
Crystallization solvent	CH_2CI_2	$CHCl_3$
number of column axes (and angle between them)	2 (85.9°)	2 (7.8°)
Angles between $C_{\scriptscriptstyle 18}$ and Ar (°)	8.1-19.8	12.9-30.8
distance between closest $C_{\scriptscriptstyle 18}$ mean planes (Å)	3-39	-
shortest C-C distance between $C_{\scriptscriptstyle 1B}$ rings	3.37	3.60
columnar verticality deviation (°). $^{ m b}$	57-3	-
shortest distance between a $^t\text{Bu}\text{H}$ and a $C_{\scriptscriptstyle 18}\text{mean}$	1.67	0.89
plane (centroid) (Å)	(1.88)	(1.20)

^a See reference [12]. ^b "Verticality deviation" is angle between the column axis and the normal to the mean planes of the constituting macrocycles.

The *carbo*-benzene **2b**, with 3 different pairs of substituents (Ph, ^FTol, ^tBu) is a strong chromophore, just as **1a**, **1b** and **2a**, appearing as dark violet in the solid state, and giving violet solutions in organic solvents. The UV-vis absorption profiles of **2b** and **1b** are identical (Figure 3), with a 5 nm red shift for **2b** ($\lambda_{max} = 452$ nm) vs **1b** ($\lambda_{max} = 447$ nm). Likewise, a 6 nm red shift is

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observed for **2a** (λ_{max} = 478 nm in THF) vs **1a** (λ_{max} = 472 nm in CHCl₃: in the *carbo*-benzene series, solvatochromism has indeed been reported to be very weak).^[27] The electron-withdrawing character of the CF₃ groups of **2b** has thus a minor effect, in qualitative agreement with the relative average HOMOS-LUMOS gap: ($E_{LUMO+1} + E_{LUMO} - E_{HOMO} - E_{HOMO-1}$)/2 \approx 0.091 au for both **1b** and **2b** (see Supporting Information, Figure S2). The ε value of **2b** (120 000 L.mol⁻¹.cm⁻¹) was measured to be three times lower than that of its analog **1b** (350 000 L.mol⁻¹.cm⁻¹), but also two times lower than that of **1a** (230 000 L.mol⁻¹.cm⁻¹) (see Supporting Information, Figure S3).



Figure 3. Normalized UV-vis absorption spectra of the ditertiobutyl-diphenyl-*carbo*benzene derivatives **1b**, **2b** and their tetraphenyl analogues **1a** and **2a**.

A more significant effect of the CF_3 groups is observed on the redox behavior, as indicated from square-wave voltammetry (SWV) and cyclic voltammetry (CV) measurements of **2b** and **1b** (Table 2).

Table 2. SWV and CV data for the *carbo*-benzene **2b** and its tetraphenyl-di-*tert*-butyl counterpart **1b**.^[a]

	Reduction			Oxidation		
	E _{1/2} ^[b]	<i>RI</i> _p ^[d]	$E_{p}^{red[e]}$	E _{1/2} ^[b]	$RI_p^{[d]}$	Ep ^{ox[e]}
	$(\Delta E_p)^{[c]}$			$(\Delta E_p)^{[c]}$		
2b	- 0.76 (63)	0.95		-	-	1.28
	- 1.10 (59)	0.80				1.52
			-			1.76
1b ^[4]	- 0.88 (73)	0.99		-	-	1.18 ^[f]
	- 1.31 (73)	0.85				1.72
			- 1.96			2.00

^[a] Measurements in CH₂Cl₂ solutions at r. t.; supporting electrolyte: [*n*Bu₄N][PF₆] (o.1 M); working electrode: Pt; reference electrode: saturated calomel electrode (SCE; o.242 V vs the hydrogen electrode); scan rate: o.2 V s⁻¹ unless otherwise noted. ^[b] Halfwave potential, $E_{1/2} = (E_p^{red} + E_p^{ox})/2$, in V vs SCE. ^[c] Separation between the two peak potentials: $\Delta E_P = |E_p^{red} - E_p^{ox}|$, in mV. ^[d] Peak current ratio $RI_p = |I_p^{ox}|/p^{red}$]. ^[e] E_p values measured from SWV in V vs SCE. ^[f] Reversibility observed at high scan rate (5 V s⁻¹). As expected, and supported by the near-frontier orbital levels of **2b** vs **1b** (generalized for **2a** vs **1a**: see Supporting Information, Figure S2), the bis(trifluorotolyl)-*carbo*-benzene **2b** is "easier" to reduce and more "difficult" to oxidize than **1b**. While three reduction waves were described for **1b**, two reversible waves are observed for **2b** at – 0.76 and – 1.10 V (vs – o.88 V and – 1.31 V for **1b**). The electron accepting effect of the CF₃ groups is however partially compensated by the σ -donating effect of the two ¹Bu substituents, the first reduction of hexaphenyl-*carbo*-benzene **1a** occurring at a slightly higher potential of –0.72 V (*vs* –0.76 V for **2b**).^[11] In the oxidation regime, three waves are observed for both **2b** and **1b**, the first process occurring at a higher potential for **2b** (E_p^{ox} (**2b**) = +1.28 V, E_p^{ox} (**1b**) = +1.18 V). These variations in redox potentials are in agreement with the shifts of the LUMO level (–0.116 au for **2b** *vs* –0.104 au for **1b**) and HOMO level (–0.203 au for **2b** *vs* –0.192 au for **1b**).

The molecular 2D-packing of **2b** was investigated on a highly oriented pyrolytic graphite (HOPG) surface (Figure 4): STM images show an ordered monolayer along two "horizontal" (in-plane) orientations. The "vertical" orientation is however found variable, the molecular mean planes being more or less tilted on the HOPG surface, leant molecules of **2b** partially overlapping one another. In a few regions, "horizontal" molecules are however observed, the planar C_{18} core stacking face-to-face with the substrate (Figure 4c).^[28,29] Figures 4b and 4d suggest that the molecular alignment is oriented by the CF₃ groups.^[30] The Autocorrelation Function (ACF) of Figure 4b) reveals the lattice vectors of the self-assembly and the separation distance between neighboring molecules (Figure 4e).



Figure 4. a) (*top left*) Large-area STM image of self-assembled **2b** (*lt* = 100 pA, *U* = 0.95 V). b) (*top right*) Smaller area STM image (*lt* = 110 pA, *U* = 0.9 V). c) (*middle*) STM image of a region where molecules **2b** adhere on the HOPG surface by "horizontal" π -stacking of their C₁₈ core. d) (*bottom left*) High-resolution STM image showing the self-assembly (*lt* = 80 pA, *U* = 1.05 V). e) (*bottom right*) Lattice parameters using Autocorrelation Function (ACF, Gwyddion software) on the STM image 4b. Conditions: substrate: HOPG; solvent: 1-phenyloctane; concentration: *ca*. 0.1 mM; liquid/solid interface @RT; equipment: Nanosurf STM.

The bistrifluorotolyl *carbo*-benzene **2b** was finally tested in organic photovoltaic (OPV) cells as either electron acceptor or electron donor vs the standard P₃HT or PC₇₁BM counterpart, respectively. ^[31-33] The used active layers were deposited by spin coating from corresponding binary solutions

in chloroform or chlorobenzene. With respect to the reference OPV system P₃HT:PC₇₂BM, *J-V* plots of the fabricated systems P₃HT:**2b** and **2b**:PC₇₂BM revealed a negligible photo-conversion efficiency. In these experiments, however, the absence of photovoltaic performance of **2b** can be at least partly imputed to the roughness of the films (rms \approx 7 nm): this is clearly indicated by comparison of optical microscopy and AFM images of the films with those of the much more regular P₃HT:PC₇₂BM films (rms \approx 1 nm; see Figure S1b-d). The film inhomogeneity can be ultimately attributed to a still insufficient solubility of **2b**, which, upon mixing with P₃HT, can result in a partial separation of the chemical components during spin coating. Optimization of the deposition process is therefore needed.

Conclusions

Peripheral fluorination of the carbo-benzene ring has been addressed in a systematic manner from the hexaphenyl and ditertiobutyltetraphenyl hydrocarbon references 1a and 1b. Although delineation of possible prospects of application require further work, the gained observations provide guidelines for structural optimization, in particular regarding the issue of solubility vs polarity around the wide C_{18} macrocycle. Replacement of the trifluorotolyl groups of 2a and 2b by pentafluorophenyl groups could be naturally envisaged, while remaining aware of the challenge of the final reductive aromatization of the corresponding [6]pericyclynediol which might be prevented by C_6F_5 substituents just as it is by CF_3 counterparts:^[19] ^{21]} the electron-withdrawing effects of C₆F₅ is indeed just slightly weaker than that of CF_3 , itself slightly weaker than that of F_2 .^[34] The polarity and solubility, and thus photovoltaic properties of thin films, could also be altered by quitting the dipolar/quadrupolar p-difluorination patterns of 2a and **2b**, for octupolar trifluorination patterns or even quadrupolar hexafluorination patterns (as a model, hexafluoro-carbo-benzene C18F6 was calculated to be stable, with very low first multipolar characteristics). [35] Further computational and experimental investigations along these lines are under current progress.

Experimental Section

General remarks

Solvents were dried with a PureSolv-MD-5 Innovative Technology system for the purification of solvents. All other reagents were used as commercially available. In particular, *n*-BuLi were 1.6 or 2.5 M in hexane, EtMgBr was 3 M in THF, HCl was 2 M in diethyl ether, LiHMDS was 1 M in THF, and ethynylmagnesium bromide was 0.5 M in THF. All reactions were carried out under argon atmosphere using Schlenk and vacuum lines techniques. Column chromatography was carried out on silica gel (60 Å, C.C 70-200 μ m). Silica gel thin layer chromatography plates (60F254, 0.25 mm) were revealed under UV-light and/or by treatment with an ethanolic solution of phosphomolybdic acid (20 %). The following analytical instruments were used, ³H, ³⁹F and ³³C NMR: Avance 400, Avance 300, Avance 400 HD and Avance NEO 600 MHz spectrometers; mass spectrometry: TSQ 7000 Thermo Electron and Voyager DE-ST Perseptive Biosystems spectrometers; UV-visible: Perkin-Elmer UV-vis Win-Lab Lambda 35; IR: Perkin Elmer 1725. NMR chemical shifts are given in ppm with positive values to high frequency relative to the tetramethylsilane reference. Coupling constants *J* are in Hertz. UV-visible extinction molar coefficient ε is in L.mol⁻¹.cm⁻¹ and wavelengths λ are in nm.

Synthesis procedures and characterization of all new compounds

1,4,10,13-tetraphenyl-7,16-bis(4-(trifluoromethyl)phenyl)cycloocta-

deca-1,2,3,7,8,9,13,14,15-nonaen-5,11,17-triyne (2a). A partially purified sample of 3a (0.150 g, ca 0.15 mmol) in DCM (100 mL) was treated at -78 °C with SnCl₂ (0.30 g, 1.54 mmol) and HCl (1.54 mL, 3.08 mmol). The resulting mixture was stirred for 20 minutes at -78 °C and for 1 h at room temperature (r. t.), before treatment with 1M aqueous NaOH (3.08 mL, 3.08 mmol). After extractions with DCM, the combined organic layers were washed with brine, dried over MgSO₄ and concentrated under reduced pressure. Purification by silica gel chromatography (pentane/DCM 8:2) followed by washings with pentane and DCM afforded 15 mg of a poorly soluble grey powder containing 2a as main product. This very low solubility only allowed partial characterization of 2a.

M.p.: 170°C.

^aH NMR (600 MHz, THF- d_8) δ 7.92 (t, J = 7.2 Hz, 4H, p- C_6H_5), 8.19 (t, J = 7.5 Hz, 8H, m- C_6H_5), 8.52 (d, J = 7.9 Hz, 4H, m- C_6H_4), 9.63 (d, J = 7.5 Hz, 8H, o- C_6H_5), 9.80 (d, J = 7.9 Hz, 4H, o- C_6H_4).

¹⁹F NMR (282 MHz, THF- d_8) δ -65.03.

UV-vis (THF): λ_{max} = 478 nm (due to an extremely low solubility, the molar extinction coefficient ε could not be determined).

HRMS (MALDI-TOF/DCTB): m/z calculated for $C_{56}H_{29}F_6$ [M]⁺: 814.216, found 814.209.

1,16-di-tert-butyl-7,10-diphenyl-4,13-bis(4-(trifluoromethyl)phenyl) cyclooctadeca-1,2,3,7,8,9,13,14,15-nonaen-5,11,17-triyne (2b). The partially purified sample of 3b (0.120 g, ca 0.13 mmol) in DCM (80 mL) was treated at – 78 °C with SnCl₂ (0.24 g, 1.30 mmol) and HCl (1.29 mL, 2.60 mmol). The resulting mixture was stirred for 1.5 h at – 78 °C and for 15 minutes at r. t., before treatment with 1M aqueous NaOH (2.58 mL, 2.58 mmol). After extractions with DCM, the combined organic layers were washed with brine, dried over MgSO₄ and filtered through celite® before

concentration under reduced pressure. Purification by silica gel chromatography (pentane/DCM 9:1) followed by washings with pentane and DCM afforded **2b** as a violet powder (0.060 g, 20 % from **5** and **4b**).

M.p.: 161°C. ¹H NMR (600 MHz, CDCl₃) δ 2.53 (s, 18H, ⁶Bu), 7.76 (t, J = 7.2 Hz, 2H, p-C₆H₅), 8.03 (t, J = 7.5 Hz, 4H, m-C₆H₅), 8.26 (d, J = 7.9 Hz, 4H, m-C₆H₄), 9.51 (d, J = 7.5 Hz, 4H, o-C₆H₅), 9.64 (d, J = 7.9 Hz, 4H, o-C₆H₄). ¹³C NMR (151 MHz, CDCl₃) δ 33.1, 41.9, 101.4, 104.4, 113.8, 116.5, 116.9, 118.3, 118.9, 120.7, 121.0, 123.9, 124.4 (q, J = 272 Hz), 126.7, 129.6, 130.1, 130.7, 130.8 (q, J = 33Hz), 140.3, 143.8. ¹³F NMR (282 MHz, CDCl₃) δ - 62.4. HRMS (MALDI-TOF/DCTB+Nal): m/z calculated for C₅₂H₃₆F₆ [M⁺]: 774.276, found 774.272. UV-vis (CHCl₃): $\lambda_{max} = 452$ nm (ϵ = 120 000 L/mol/cm).

4,7,13,16-tetramethoxy-4,7,13,16-tetraphenyl-1,10-bis(4-(trifluoro methyl)phenyl)cyclooctadeca-2,5,8,11,14,17-hexayne-1,10-diol (3a). A solution of 4a (0.070 g, 0.22 mmol) in THF (10 mL) was treated at - 78 °C with LiHMDS (1.32 mL, 1.32 mmol). The resulting mixture was stirred for 30 minutes. This solution was then added simultaneously with a solution of 5 (0.144 g, 0.22 mmol) in THF (10 mL) through cannula into a flask containing THF (200 mL) under stirring at – 78 °C. The resulting mixture was allowed to warm slowly to r. t. under stirring overnight, and then treated with a saturated aqueous solution of NH₄Cl. The aqueous layer was extracted several times with diethyl ether, and the combined organic layers were washed with brine, dried with MgSO4 and concentrated under reduced pressure. A purification by silica gel chromatography (pentane/Et2O 95:5) afforded 0.140 g of a brown paste which was used in the next step without further purification. The formation of 3a was however confirmed by mass spectrometry: HRMS (DCI-CH₄): m/z calculated for C₆₀H₄₁O₅F₆ [M-H₂O+H]⁺: 955.2896, found: 955.2858

4,7-di-tert-butyl-4,7,13,16-tetramethoxy-13,16-diphenyl-1,10-bis(4-(trifluoromethyl)phenyl)cyclooctadeca-2,5,8,11,14,17-hexayne-1,10-

diol (3b). A solution of 4b (0.110 g, 0.4 mmol) in THF (20 mL) was treated at - 78 °C with LiHMDS (2.4 mL, 2.4 mmol). The resulting mixture was stirred for 30 minutes before addition of THF (30 mL). This solution was then added simultaneously with a solution of 5 (0.264 g, 0.4 mmol) in THF (50 mL) through canula into a flask containing THF (300 mL) under stirring at -78 °C. The resulting mixture was allowed to warm slowly to r. t. under stirring overnight, and then treated with a saturated aqueous solution of NH₄Cl. The aqueous layer was extracted several times with diethyl ether, and the combined organic layers were washed with brine, dried with MgSO4 and concentrated under reduced pressure. A purification by silica gel chromatography (pentane/DCM/acetone 2:1:0.5) afforded 0.120 g of a brown paste mainly containing **3b**, which was used in the next step without further purification. Although it was not isolated in the pure state, the formation of **3b** was supported by ¹H NMR and mass spectrometry analyses. ¹H NMR (300 MHz, CDCl₃) δ 1.10 – 1.32 (m, 18H, ^tBu), 2.5 (2s, 2H, OH), 3.25 -3.67 (m, 12H, O-CH₃), 7.27 - 7.48 (m, 6H, p-C₆H₅, m-C₆H₄), 7.53 - 8.02 (m, 12H, o-C₆H₄, o-C₆H₅, m-C₆H₅). MS (MALDI-TOF LD+, DCTB/NaI), among unidentified peaks: $m/z = 901.3 ([M - MeO]^{+}), 899.4 ([M - MeO - H]^{+}: H^{+})$ possibly eliminated from a ^tBu group, resulting in the putative formation of a dimethylcyclopropylium).

4,7-dimethoxy-4,7-diphenyl-1,10-bis(4-(trifluoromethyl)phenyl)deca-

2,5,8-triyne-1,10-dione (5). A solution of **6** (0.650 g, 0.98 mmol) in DCM (30 mL) was treated with MnO2 (2.5 g, 29.4 mmol) at 0 °C. The mixture was stirred for 1 h at 0 °C and 5 h at r. t., before filtration through celite® and concentration under reduced pressure to afford **5** as a spectroscopically pure yellow oil (0.55 g, 85%).

¹H NMR (400 MHz, CDCl₃) δ 3.69 (25, 6H, -OCH₃), 7.49 (m, 6H, *m*-, *p*- C₆H₅), 7.74 (m, 4H, *o*- C₆H₅), 7.85 (m, 4H, *o*- C₆H₄), 8.22 (m, 4H, *m*- C₆H₄). ¹³C NMR (101 MHz, CDCl₃) δ 54.0, 72.1, 83.2, 84.5, 90.5, 123.5 (q, *J* = 274 Hz), 125.8 (m), 126.4, 128.9, 129.8 (m), 135.5 (q, *J* = 33 Hz), 138.2, 138.9, 175.7. ¹⁹F NMR (376 MHz, CDCl₃) δ -63.26 (m). HRMS (DCl-CH₄): *m/z* calculated for C₃₈H₂₄O₄F₆ [M⁺]: 658.156, found 658.157. IR: ν = 3300 (w, \equiv C-H), 2828-2935 (m, C_{sp}³-H), 2903 (w, C_{sp}²-H), 2219 (m, C \equiv C), 1656 (s, C=O), 1451 (m, C=C).

4,7-dimethoxy-4,7-diphenyl-1,10-bis(4-(trifluoromethyl)phenyl)deca-

2,5,8-triyne-1,10-diol (6). A solution of 4a (0.50 g, 1.59 mmol) in THF (20 mL) was treated with *n*-BuLi (1.4 mL, 3.49 mmol) at - 78 °C. The mixture was stirred for 15 min. at – 78 °C and for 1 h at r. t., before adding a solution of trifluoromethylbenzaldehyde (0.48 mL, 3.49 mmol) in THF (10 mL). The mixture was allowed to warm slowly up to r. t. under stirring during 12 h. After treatment with a saturated aqueous solution of NH₄Cl, the aqueous layer was extracted several times with diethyl ether and the combined organic layers were washed with brine, dried over MgSO₄ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (pentane Et₂O 95:5) to give **6** as a yellow oil (0.70 g, 66 %). ¹H NMR (400 MHz, CDCl₃) δ 2.6 (bs, 2H, OH), 3.51 (2s, 6H, OCH₃), 5.63 (s, 2H, CHOH), 7.38 (m, 6H, *m*-, *p*- C₆H₅), 7.63 (m, 8H, *o*- C₆H₅, *o*-C₆H₄), 7.75 (m, 4H, $m-C_6H_4$). ¹³C NMR (101 MHz, CDCl₃) δ 30.91 (CH₂OH), 54.34 (OCH₃), 72.31 (COMe), 84.01-90.7 (C≡C), 119.97-127.02 (CF₃), 125.57 (*p*-C₆H₅), 125.61-129.15 ($o-C_6H_5$, $m-C_6H_5$, $o-C_6H_4$, $m-C_6H_4$): due to weak signal intensities, attributable to the presence of 14 diastereoisomers, no signal is detected for quaternary ¹³C nuclei and ¹³C nuclei coupled with F atoms (C-CF₃). ¹⁹F NMR (376 MHz, CDCl₃) δ -62.63 (m). MS (DCl/CH₄): *m/z* (%): 631.16 (100) $[M + C_2H_5]^+$, 645.18 (40) $[M - C_3H_7]^+$.

Supplementary Material

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/MS-number.

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Author Contribution Statement

M. C. performed the synthesis and characterization work and wrote the corresponding experimental section. I. C.-Q. conducted the STM investigations. O. A.-R. and D. B-A. performed the photovoltaic and AFM experiments. Y. A. performed the early exploratory synthesis work. C. D. and B. K. solved the crystal structure. J. L. M. and G. R.-O. co-devised and supervised the STM, AFM and photovoltaic experiments and wrote the corresponding sections. V. M. and R. C. co-devised the work project and wrote the original main text.

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