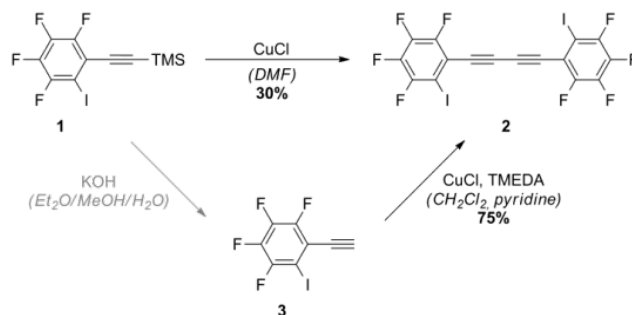


Supplementary Information

Halogen bonding and π - π interactions in the solid-state structure of a butadiynylene-linked bis(iodoperfluoroarene)

I. Synthesis



In a flame-dried flask equipped with a drying tube, 0.09 g of 1-ethynyl-2-iodo-3,4,5,6-tetrafluorobenzene **3** (0.30 mmol) were dissolved in a mixture of CH₂Cl₂ (70 mL) and pyridine (7 mL). 0.42 g of CuCl (4.24 mmol, 14 eq.) and 0.64 mL of tetramethylethylenediamine (4.24 mmol, 14 eq.) were added and the reaction mixture was stirred at room temperature for 45 h. The reaction mixture was washed with water (3 × 30 mL), dried over MgSO₄ and filtered. Removal of the solvent yielded 67.0 mg of the desired product **2** (0.11 mmol, 75%) as a brown solid.

The alternative synthetic route proceeds in the following fashion: in a flame-dried flask, 177 mg of 1-iodo-2-[(trimethylsilyl)ethynyl]-3,4,5,6-tetrafluorobenzene **1** (1 eq., 0.48 mmol) and 124 mg of CuCl (0.48 equiv, 1.25 mmol) were dissolved in 0.5 mL of DMF and stirred at 80 °C for 6 h. After the removal of the solvent, the residue was subjected to flash column chromatography (silica gel, pentane), yielding 48 mg of product **2**. (0.19 mmol, 30%).

¹⁹F-NMR (376 MHz, CDCl₃): -113.5 (m, 2F), -129.0 (m, 2F), -148.6 (m, 2F), -153.4 (m, 2F). FTIR (powder): 1618 (s), 1491 (s), 1460 (s), 948 (s), 797 (s) cm⁻¹. HRMS (EI): m/z = 697.797, calculated for C₁₆F₈I₂: 697.796.

II. Single Crystal X-Ray Structure Determination of Compound 2

General:

Data were collected on an X-ray single crystal diffractometer equipped with a CCD detector (Bruker Kappa APEX II ULTRA), a rotating anode (Bruker AXS, FR591) with MoK α radiation ($\lambda = 0.71073$ Å), and a graphite monochromator by using the SMART software package. [1] The measurements were performed on a single crystal coated with perfluorinated ether. The crystal was fixed on the top of a glass fiber and transferred to the diffractometer. The crystal was frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected

for Lorenz and polarization effects, scan speed, and background using SAINT. [2] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS. [2] Space group assignments were based upon systematic absences, *E* statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps, and were refined against all data using WinGX [7] based on SIR-92. [3] If not mentioned otherwise, non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with SHELXL-97 [5] weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*. [4] Images of the crystal structures were generated by PLATON. [6]

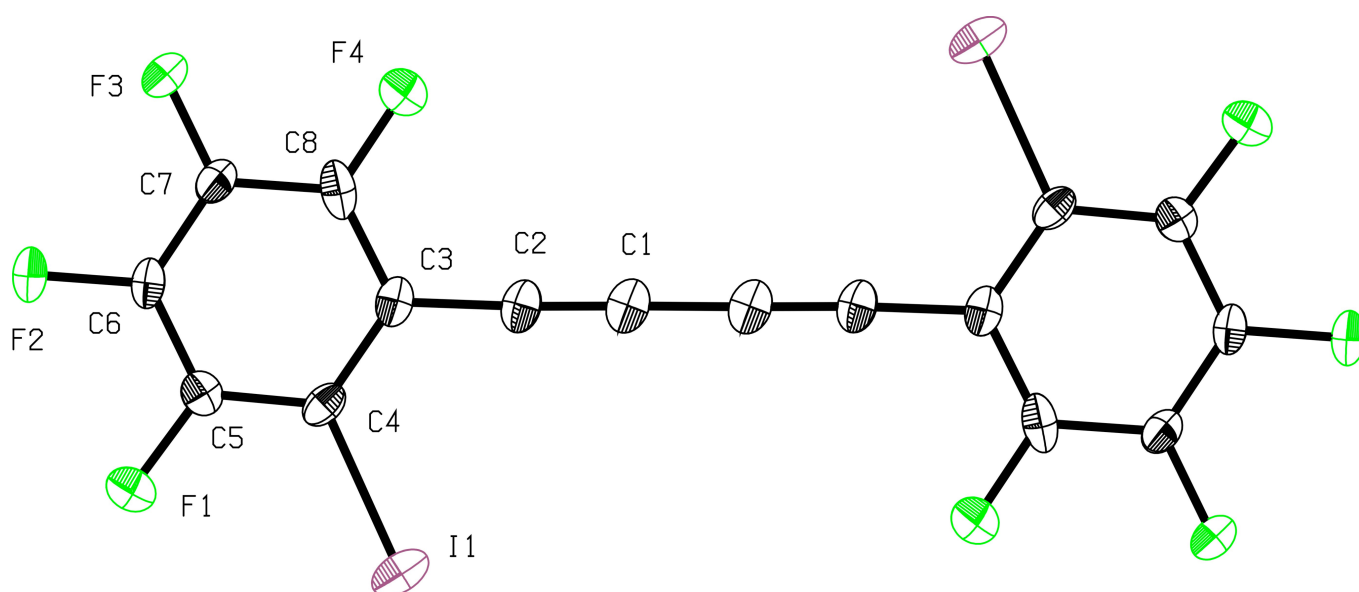


Figure S1 – Ortep drawing of compound **2** with 50% ellipsoids. [6]

Operator:	*** Herdtweck ***
Molecular Formula:	C ₁₆ F ₈ I ₂
Crystal Color / Shape	Colorless fragment
Crystal Size	Approximate size of crystal fragment used for data collection: 0.05 × 0.18 × 0.53 mm
Molecular Weight:	597.96 a.m.u.
F ₀₀₀ :	548
Systematic Absences:	h0l: l≠2n; 0k0: k≠2n
Space Group:	Monoclinic P 2 ₁ /c (I.T.-No.: 14)
Cell Constants:	Least-squares refinement of 7288 reflections with the programs "APEX suite" and "SAINT" [1,2]; theta range 1.88° < θ < 25.32°; Mo(Kα); λ = 71.073 pm a = 1182.60(5) pm b = 507.79(2) pm β = 113.431(2)° c = 1447.17(6) pm V = 797.38(6) · 10 ⁶ pm ³ ; Z = 2; D _{calc} = 2.490 g cm ⁻³ ; Mos. = 0.71
Diffractometer:	Kappa APEX II (Area Diffraction System; BRUKER AXS); rotating anode; graphite monochromator; 50 kV; 40 mA; λ = 71.073 pm; Mo(Kα)
Temperature:	(-150±1) °C; (123±1) K

Measurement Range: $1.88^\circ < \theta < 25.32^\circ$; h: -14/13, k: -6/6, l: -15/16
 Measurement Time: 2×5 s per film
 Measurement Mode: measured: 5 runs; 2016 films / scaled: 5 runs; 2016 films
 φ - and ω -movement; Increment: $\Delta\varphi/\Delta\omega = 0.50^\circ$; dx = 50.0 mm
 LP - Correction: Yes [2]
 Intensity Correction: No/Yes; during scaling [2]
 Absorption Correction: Multi-scan; during scaling; $\mu = 4.027 \text{ mm}^{-1}$ [2]
 Correction Factors: $T_{\min} = 0.5437$ $T_{\max} = 0.7452$
 Reflection Data: 9550 reflections were integrated and scaled
 582 reflections systematic absent and rejected
 8968 reflections to be merged
 1371 independent reflections
 0.028 R_{int} : (basis F_o^2)
 1371 independent reflections (all) were used in refinements
 1314 independent reflections with $I_o > 2\sigma(I_o)$
 93.7 % completeness of the data set
 118 parameter full-matrix refinement
 11.6 reflections per parameter
 Solution: Direct Methods [3]; Difference Fourier syntheses
 Refinement Parameters: In the asymmetric unit:
 13 Non-hydrogen atoms with anisotropic displacement parameters
 Atomic Form Factors: For neutral atoms and anomalous dispersion [4]
 Extinction Correction: no
 Weighting Scheme: $w^{-1} = \sigma^2(F_o^2) + (a*P)^2 + b*P$
 with a: 0.0204; b: 2.2924; P: $[\text{Maximum}(0 \text{ or } F_o^2) + 2*F_c^2]/3$
 Shift/Err: Less than 0.001 in the last cycle of refinement:
 Resid. Electron Density: $+1.07 \text{ e}_0^-/\text{\AA}^3$; $-0.69 \text{ e}_0^-/\text{\AA}^3$
 R1: $\Sigma(|F_o| - |F_c|) / \Sigma F_o$
 $[F_o > 4\sigma(F_o)]; N=1314]:$ = 0.0223
 $[\text{all reflctns}; N=1371]:$ = 0.0233
 wR2: $[\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$
 $[F_o > 4\sigma(F_o)]; N=1314]:$ = 0.0545
 $[\text{all reflctns}; N=1371]:$ = 0.0550
 Goodness of fit: $[\Sigma w(F_o^2 - F_c^2)^2 / (\text{NO} - \text{NV})]^{1/2}$ = 1.087
 Remarks: Refinement expression $\Sigma w(F_o^2 - F_c^2)^2$

III. Single Crystal X-Ray Structure Determination of Compound 6

Data were collected on a Nonius Kappa-CCD diffractometer using monochromated Mo-K α radiation and were measured using a combination of ϕ scans and ω scans with κ offsets, to fill the Ewald sphere. The data were processed using the Denzo-SMN package [8]. Absorption corrections were carried out using SORTAV [9]. The structure was solved and refined using SHELXTL V6.1 [10] for full-matrix least-squares refinement that was based on F^2 . All H atoms were included in calculated positions and allowed to refine in riding-motion approximation with U_{iso} tied to the carrier atom.

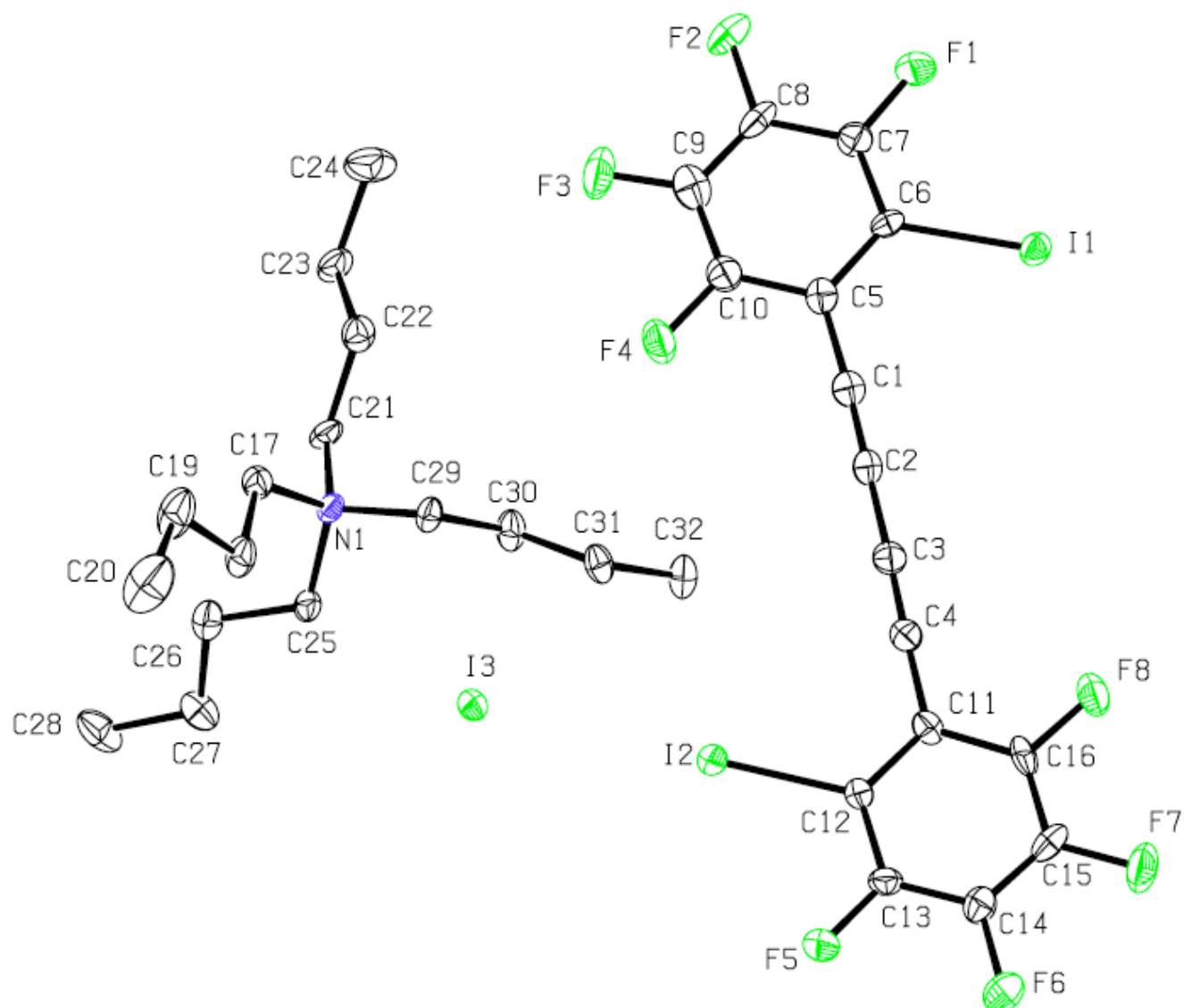


Figure S2 – Ortep drawing of compound 2 with 50% ellipsoids. [6]

Empirical formula	C ₃₂ H ₃₆ F ₈ I ₃ N
Formula weight	967.32
Temperature	150(2) K
Wavelength	0.71073 Å

Crystal system	Monoclinic
Space group	C c
Unit cell dimensions	a = 13.7911(4) Å $\alpha = 90^\circ$. b = 30.7832(10) Å $\beta = 96.2920(19)^\circ$. c = 8.3658(1) Å $\gamma = 90^\circ$.
Volume	3530.17(16) Å ³
Z	4
Density (calculated)	1.820 Mg/m ³
Absorption coefficient	2.721 mm ⁻¹
F(000)	1864
Crystal size	0.20 x 0.14 x 0.10 mm ³
Theta range for data collection	2.65 to 27.49°.
Index ranges	-17 ≤ h ≤ 17, -34 ≤ k ≤ 39, -10 ≤ l ≤ 8
Reflections collected	12445
Independent reflections	6063 [R(int) = 0.0384]
Completeness to theta = 27.49°	94.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.768 and 0.677
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6063 / 2 / 401
Goodness-of-fit on F ²	1.069
Final R indices [I > 2σ(I)]	R1 = 0.0433, wR2 = 0.0965
R indices (all data)	R1 = 0.0553, wR2 = 0.1060
Absolute structure parameter	0.51(3)
Largest diff. peak and hole	1.131 and -1.462 e.Å ⁻³

IV. Computational Details.

Calculations were carried out using the Gaussian 09 software package [11] on a Linux workstation equipped with two quad-core AMD Shanghai processors. The energy dependence on the I---I---I halogen bond angle (in the C₆F₅I---I---C₆F₅I complex) was estimated by constraining the I---I---I bond angle and optimizing the geometry at each iteration using the B3LYP functional. The 6-31G(d) basis sets were used for all atoms except iodine, for which the double- ζ LANL2DZ basis set and effective core potential (ECP) were used,[12] augmented by polarization functions of d symmetry and diffuse functions of p symmetry.[13] The LANL2DZdp basis set was downloaded from the EMSL Basis Set Exchange (<https://bse.pnl.gov/bse/portal>).[14] The I---I---I angle was incremented (and constrained) systematically by 10° from 60-170°. Stationary points were obtained at some iterations on the basis of negligible forces (Maximum force ≤ 0.000009 and RMS force ≤ 0.000002).

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