Metric engineering of perfluorocarbon-hydrocarbon layered solids driven by the halogen bonding†

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Electronic Supplementary Information
General Formation of co-crystals 3-6 involving starting materials 1a-d and 2a-b. Equimolar amounts of diiodoalkane 1a-d and the dicyano alkane 2a-b were dissolved in a vial of clear borosilicate glass at room temperature. Chloroform was used as solvent. The open vial was placed in a closed cylindrical wide-mouth bottle containing vaseline oil. CHCl₃ was allowed to diffuse at room temperature and after 24 hours co-crystals 3-6 were obtained.
X-ray diffraction analysis. Data were collected with a SMART diffractometer, Mo-Kα radiation [λ = 0.71073 Å]. The temperature was controlled by the Bruker KRIOFLEX low temperature device. All structures were refined by full-matrix least-squares on $F^2$, with anisotropic heavy atoms and isotropic H atoms.

X-ray diffraction data refinement. Structure solutions by SIR92\textsuperscript{1} and refinement on $F^2$ by SHELX97\textsuperscript{2} program packages.


3a) CCDC 230372

C$_8$H$_8$F$_4$I$_2$N$_2$, M = 461.96, monoclinic, $P2_1/n$, $a = 7.752(2)$, $b = 6.3557(14)$, $c = 12.991(3)$ Å, $β = 95.15(3)$ °, $U = 637.5(3)$ Å$^3$, $Z = 2$, $T = 90(2)$ K, $μ$(Mo-Kα) = 4.958 mm$^{-1}$, crystal dimensions 0.20x0.10x0.05; 2θ max = 72.42, 11423 reflections collected, 2935 unique, 2246 with $I > 2σ(I)$, $R_{ave} = 0.0508$, absorption corrections: Tmin/Tmax=0.582. 89 parameters refined, final $R$(all) = 0.0684, $R$(obs) = 0.0464, wR = 0.0904, G.o.F. 1.012, difference Fourier residues -2.24 < ρ < 3.04 eÅ$^{-3}$.

6a) CCDC 230373

C$_{14}$H$_8$F$_{16}$I$_2$N$_2$, M = 762.02, triclinic, $P(-1)$, $a = 5.3349(6)$ b = 7.3918(8)), $c = 14.6816(18)$ Å, $α = 93.480(14)$ $β = 97.835(15)$ $γ = 110.882(13)$ °, $U = 532.13(11)$ Å$^3$, $Z = 1$, $T = 90(2)$ K, $μ$(Mo-Kα) = 3.099 mm$^{-1}$, crystal dimensions 0.29x0.22x0.12; 2θ max = 72.38, 15685 reflections collected, 4825 unique, 4625 with $I > 2σ(I)$, $R_{ave} = 0.0247$, absorption corrections: Tmin = 0.565, Tmax=0.680. 170 parameters refined, final $R$(all) = 0.352, $R$(obs) = 0.0332, wR = 0.0791, G.o.F. 1.199, difference Fourier residues -1.31 < ρ < 2.44 eÅ$^{-3}$. 
4a) CCDC 230374

C_{10}H_{8}F_{8}I_{2}N_{2}, M = 561.98, triclinic, P(-1), a = 5.2447(5), b = 7.9197(6), c = 9.6803(10) Å, α = 84.078(12), β = 85.711(11), γ = 75.147(9) °, U = 386.09(6) Å³, Z = 1, T = 90(2) K, μ(Mo-Kα) = 4.152 mm⁻¹, crystal dimensions 0.19x0.13x0.10; 2θ_max = 72.36, 14301 reflections collected, 3586 unique, 3427 with I > 2σ(I), R_ave = 0.0209, absorption corrections: Tmin = 0.563, Tmax=0.660. 116 parameters refined, final R(all) = 0.0201, R(obs) = 0.0184, wR = 0.0448, G.o.F. 1.068, difference Fourier residues -0.63 < ρ < 1.41 eÅ⁻³.

5a) CCDC 230375

C_{12}H_{8}F_{12}I_{2}N_{2}, M = 662.00, triclinic, P(-1), a = 5.3183(8), b = 7.0369(11), c = 13.415(2) Å, α = 75.865(8), β = 86.012(12), γ = 71.855(9) °, U = 462.63(12) Å³, Z = 1, T = 90(2) K, μ(Mo-Kα) = 3.515 mm⁻¹, crystal dimensions 0.30x0.20x0.11; 2θ_max = 71.86, 11424 reflections collected, 4056 unique, 3722 with I > 2σ(I), R_ave = 0.0271, absorption corrections: Tmin = 0.559, Tmax=0.670. 143 parameters refined, final R(all) = 0.0446, R(obs) = 0.0388, wR = 0.1029, G.o.F. 1.137, difference Fourier residues -2.32 < ρ < 2.71 eÅ⁻³.

4b) re107 CCDC 230376

C_{12}H_{12}F_{8}I_{2}N_{2}, M = 590.04, monoclinic, P2₁/n, a = 7.8842(8), b = 6.3141(6), c = 17.377(2) Å, β = 92.886(8) °, U = 863.96(16) Å³, Z = 2, T = 90(2) K, μ(Mo-Kα) = 3.717 mm⁻¹. crystal dimensions 0.16x0.11x0.04. 2θ_max = 72.82, 17631 reflections collected, 4048 unique, 3553 with I > 2σ(I), R_ave = 0.0359, absorption corrections: Tmin/ Tmax = 0.824, 133 parameters refined, final R(all) = 0.0419, R(obs) = 0.0344, wR = 0.0728, G.o.F. 1.091, difference Fourier residues -1.88 < ρ < 1.80 eÅ⁻³.

5b) CCDC 230377

C_{14}H_{12}F_{12}I_{2}N_{2}, M = 690.06, triclinic, P(-1), a = 5.2409(6), b = 9.7393(9), c = 10.3874(102) Å, α = 79.665(10), β = 76.972(11), γ = 84.691(10) °, U = 507.42(9) Å³, Z = 1, T = 90(2) K, μ(Mo-Kα) =
3.209 mm\(^{-1}\), crystal dimensions 0.28x0.16x0.13; \(2\theta_{\text{max}} = 72.48\), 4644 unique, 4351 with \(I > 2\sigma(I)\), absorption corrections: Tmin = 0.501, Tmax=0.607. 160 parameters refined, final \(R(\text{all}) = 0.0214\), \(R(\text{obs}) = 0.0195\), \(wR = 0.0489\), G.o.F. 1.051, difference Fourier residues -1.15 < \(\rho\) < 1.24 eÅ\(^{-3}\).

6b) CCDC 230378

\(\text{C}_{16}\text{H}_{12}\text{F}_{16}\text{I}_{2}\text{N}_{2}\), \(M = 790.08\), triclinic, \(P(-1)\), \(a = 5.4008(16)\), \(b = 7.214(2)\), \(c = 16.065(4)\) Å, \(\alpha = 88.713(8)\), \(\beta = 87.854(6)\), \(\gamma = 72.453(10)\) °, \(U = 596.3(3)\) Å\(^3\), \(Z = 1\), \(T = 200(2)\) K, \(\mu(\text{Mo-K}\alpha) = 2.769\) mm\(^{-1}\), crystal dimensions 0.22x0.13x0.04; \(2\theta_{\text{max}} = 55.22\), 10182 reflections collected, 2756 unique, 2116 with \(I > 2\sigma(I)\), \(R_{\text{ave}} = 0.0425\), no absorption corrections. 187 parameters refined, final \(R(\text{all}) = 0.0431\), \(R(\text{obs}) = 0.0338\), \(wR = 0.0712\), G.o.F. 0.876, difference Fourier residues -0.42 < \(\rho\) < 0.93 eÅ\(^{-3}\).
**Figure 3** Crystal packing of 5a viewed down the $b$ crystallographic axis.
Figure 4 Crystal packing of 4b viewed down the a crystallographic axis.
Figure 5 Crystal packing of 5b viewed down the b crystallographic axis.
Figure 6 Crystal packing of 6b viewed down the $b$ crystallographic axis.
**Figure 7** Crystal packing of 3a viewed down the a crystallographic axis.
**Figure 8** Crystal packing of 6a viewed down the *b* crystallographic axis.
Figure 9 Crystal packing of 4a viewed down the $b$ crystallographic axis.