Electronic Supplementary Material (ESI) for ChemComm.


# Supporting Information for

## Sterically Crowded 1,4-Diiodobenzene as Precursor to Difunctional Hypervalent Iodine Compounds

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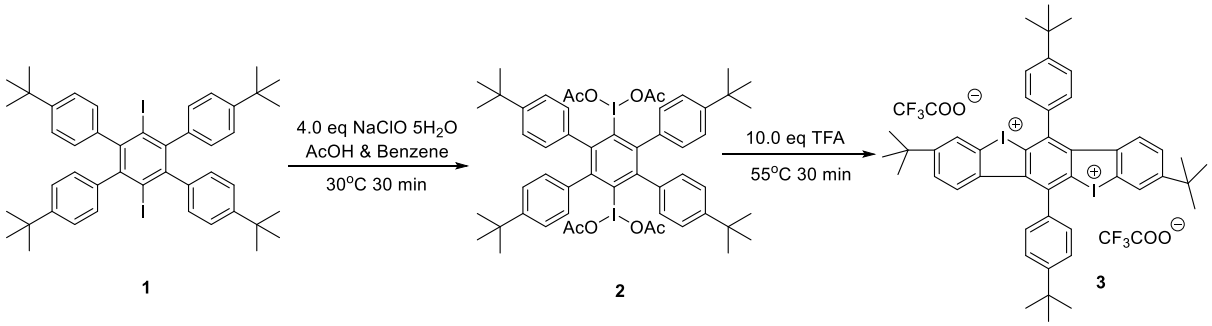
## Contents

# Experiment Procedures

**General Information**. All starting materials, reagents, and solvents were purchased from commercial sources and used without further purification. $^{1}$H NMR and $^{13}$C {$^{1}$H} NMR spectra were obtained on Bruker Avance III HD 500 MHz NMR Spectrometer. Chemical shifts (δ) are reported in parts per million (ppm). Melting points were determined with melting points apparatus and are uncorrected.

**Method**: As shown in **Scheme 1**, the unusual 1,4-diiodobenzene (**1**) bearing four *para*-$^{t}$Bu-$C_6H_4$ groups was prepared according to our previous paper.[1] **1** was then oxidized into (diacetoxyiodo)iodoarenes (**2**) through sodium hyperchlorite pentahydrate.[2] **2** was expected to react with trifluroacetic acid (TFA) to synthesize [bis(trifluoroacetoxy)iodoarenes], but it was cyclized to form iodonium salts to give compound **3**.




**Scheme S1.** Synthesis of hypvervalent iodine with di-iodine(III) centers compounds **2** and **3**.

**2,3,5,6-tetra-terbutylphenyl-1,4-(diacetoxyiodo)benzene** (**2**): Sodium hyperchlorate pentahydrate (1.32 g, 4.0 mmol) and compound **1** (0.858 g, 1.0 mmol) were added into a 50 mL flask with a stir bar. Glacial acetic acid (10 mL) and benzene (10 mL) were added and stirred at 30°C for 30 min. Concentrated to remove the solvent and extracted with DCM. Dried over $Na_2SO_4$ and concentrated to obtain white solid. Crystals were obtained from slow evaporation of DCM. Yield: 0.81 g, 73.9%. Melting points: greater than 350 °C. $^{1}$H NMR (500 MHz, Chloroform-d) δ = 7.12 (s, 2H), 7.01 (d, J = 8.0 Hz, 2H), 1.98 (s, 3H), 1.20 (s, 9H). $^{13}$C {$^{1}$H} NMR (126 MHz, Chloroform-d) δ= 176.30, 151.47, 146.84, 139.33, 137.05, 129.29, 124.24, 34.66, 31.28, 20.69.

**2,6,7,10-tetra-terbuytl-bisdibenziodolium trifluroacetate (3):** Compound **2** (1.09 g, 1.0 mmol) and TFA (10.0 eq, 0.77 mL) were added into a 50 mL flask with a stir bar. The mixture was stirred at 50°C for 30 min and cooled down to room temperature. DI water (30 mL) was added and the mixture was extracted with DCM. Dried over $Na_2SO_4$ and concentrated to obtain the solid. Crystals were obtained from vapor diffusion (hexanes into a solution of **3** in DCM). Yield: 0.42 g, 38.8%. Melting points: greater than 350 °C. $^{1}$H NMR (500 MHz, Chloroform-*d*) δ = 8.39 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 1H), 6.74 (d, *J* = 8.6 Hz, 1H), 1.51 (s, 9H), 1.30 (s, 9H).$^{13}$C {$^{1}$H} NMR (126 MHz, Chloroform-d) δ= 162.24,161.95, 161.66, 161.37, 156.85, 155.70, 141.35, 138.06, 137.53, 137.13, 135.53, 130.33, 128.76, 128.37, 127.46, 123.30, 117.16, 114.84, 36.03, 35.51, 31.42, 30.90. $^{19}$F {$^{1}$H} NMR (471 MHz, Chloroform-*d*) δ= -75.61.

# NMR Spectra

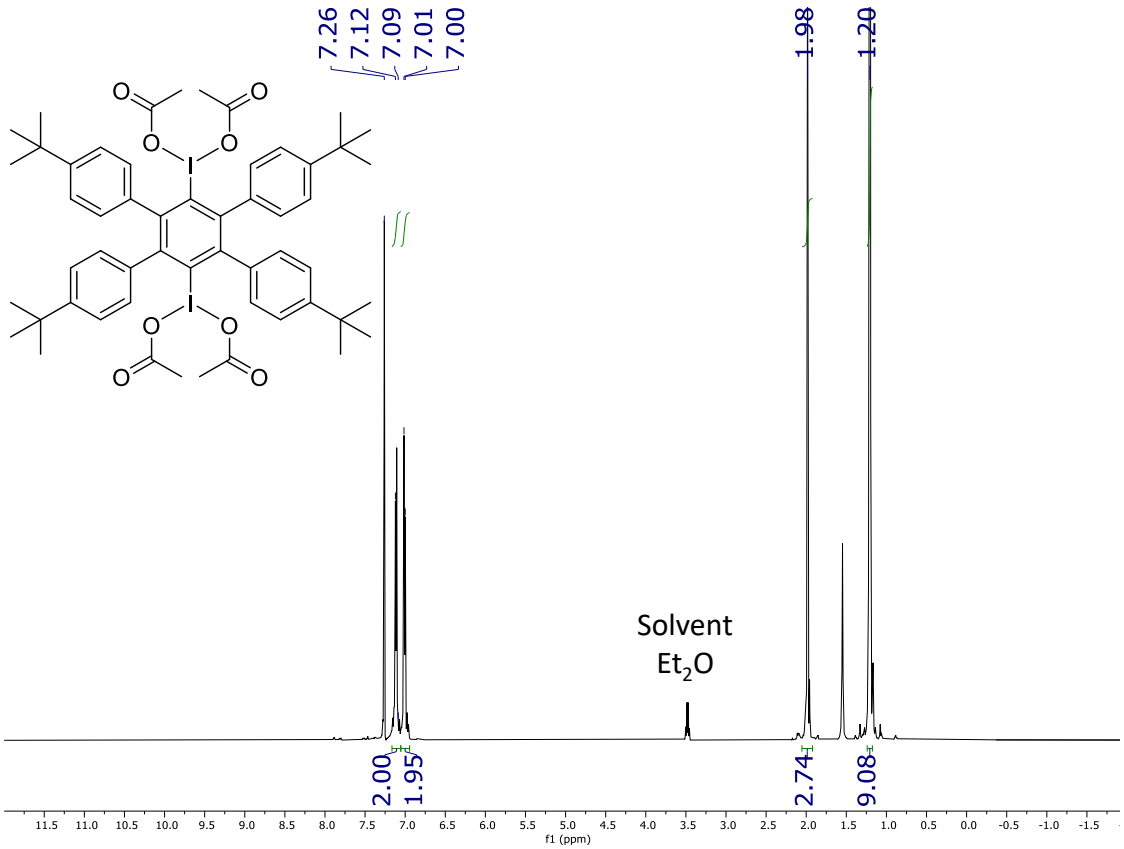



**Figure S1.** $^{1}H$ NMR spectrum of 2 ($CDCl_3$, 500 MHz, 298K)

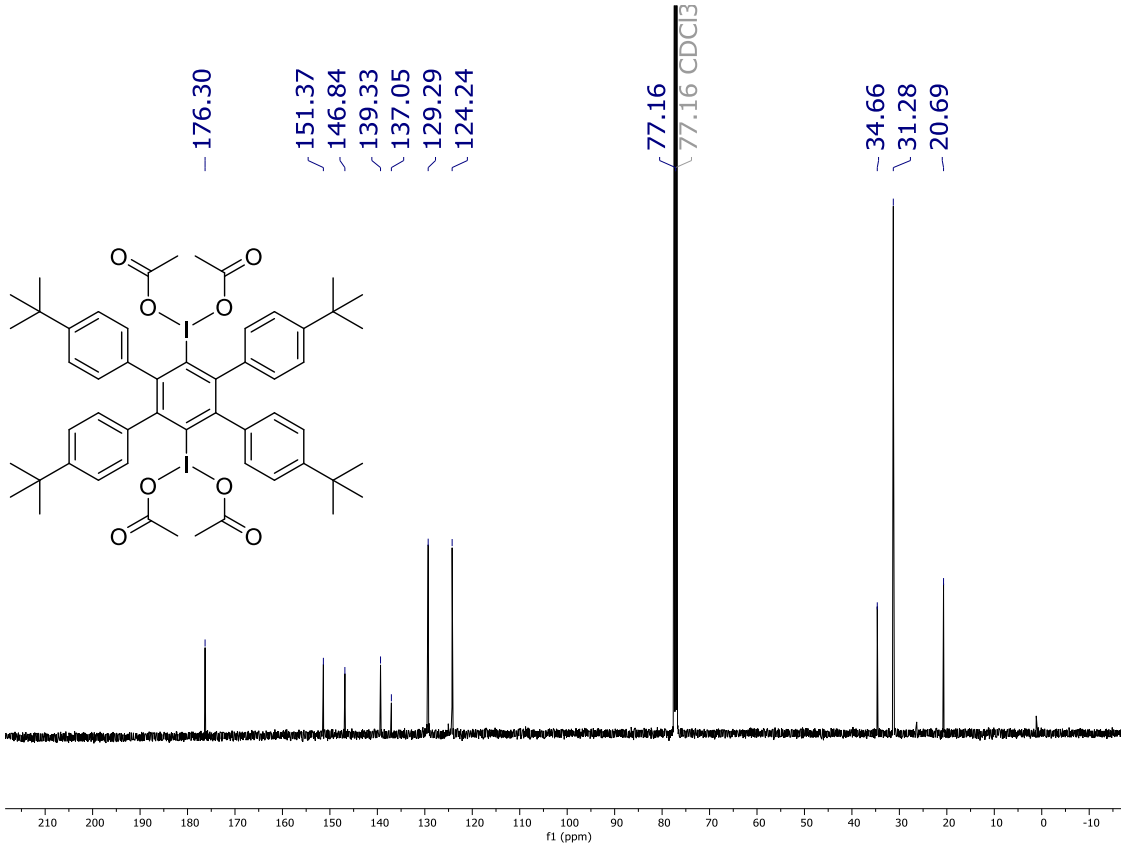



**Figure S2.** $^{13}C$ {$^{1}H$} NMR spectrum of 2 ($CDCl_3$, 126 MHz, 298K)

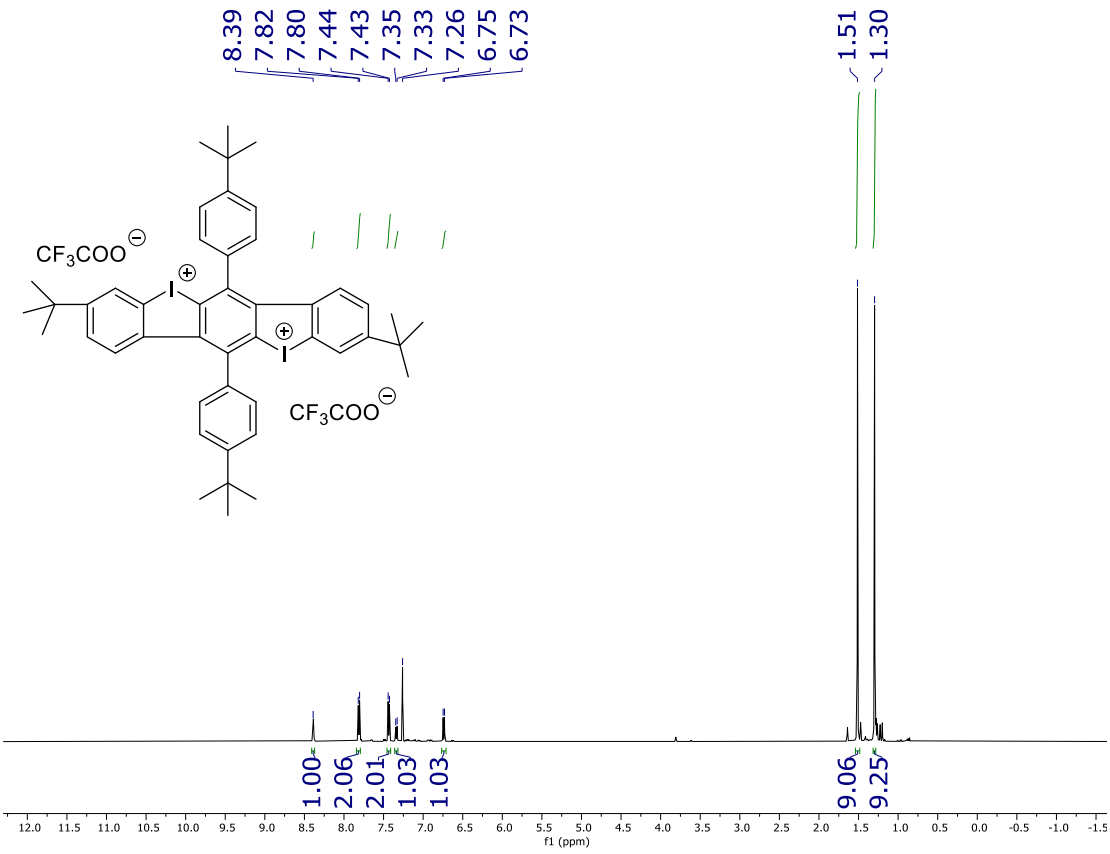



**Figure S3.** $^{1}H$ NMR spectrum of 3 ($CDCl_3$, 500 MHz, 298K)

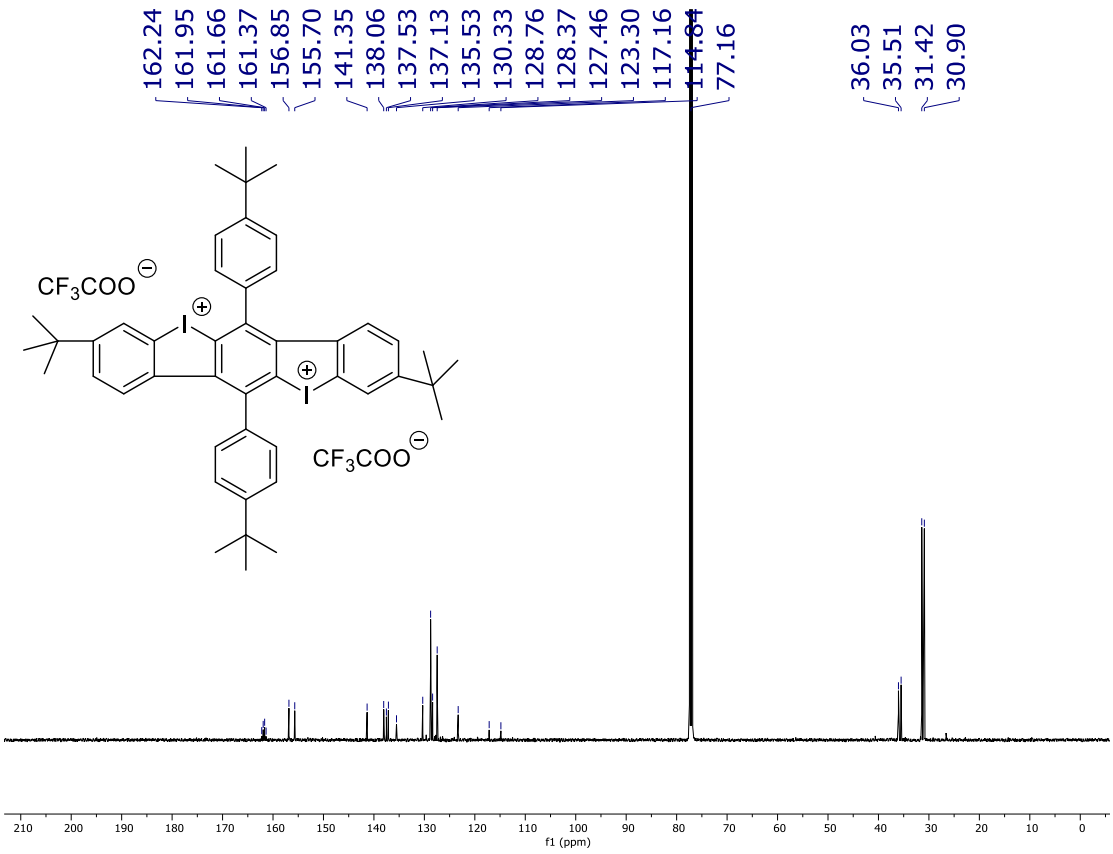



**Figure S4.** $^{13}C$ $\{^{1}H\}$ NMR spectrum of **3** ($CDCl_3$, 126 MHz, 298K)

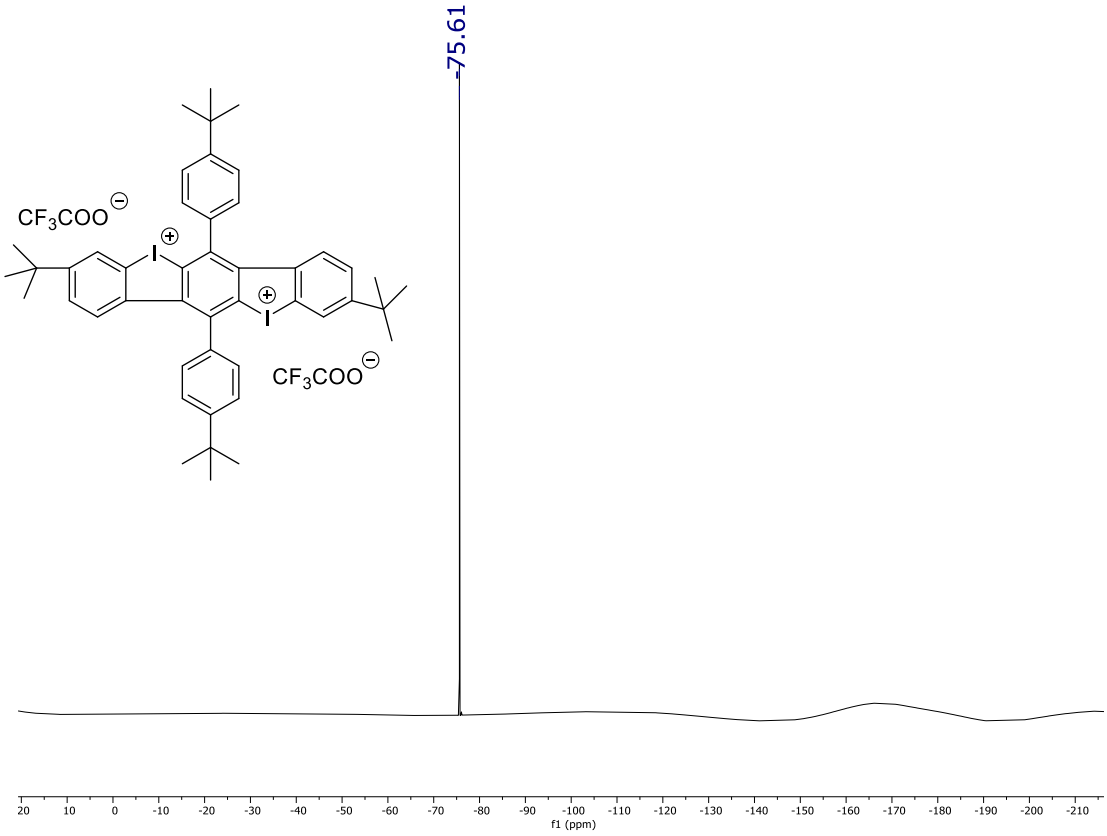



**Figure S5.** $^{19}F$ $\{^{1}H\}$ NMR spectrum of **3** ($CDCl_3$, 471 MHz, 298K)

# Crystallographic Analysis

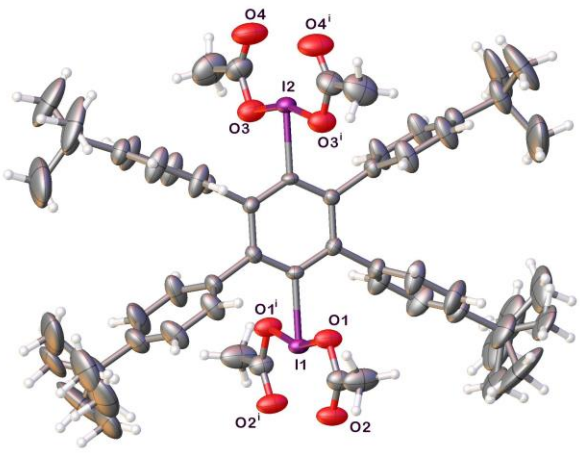



**Figure S5.** Structural diagram of compound **2**.

**Table S1**. Crystal data and structure refinement for compound **2**_200K_sq.

| | | |
|---|---|---|
| Identification code | compound **2** | |
| Empirical formula | $C_{54}$ $H_{64}$ $I_2$ $O_8$ | |
| Formula weight | 1094.85 | |
| Temperature | 100.0 K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | Pnna | |
| Unit cell dimensions | a = 21.9600(4) Å | □= 90°. |
| | b = 15.2357(3) Å | □= 90°. |
| | c = 18.1317(4) Å | □ = 90°. |
| Volume | 6066.4(2) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.199 $Mg/m^3$ | |
| Absorption coefficient | 1.080 $mm^{-1}$ | |
| F(000) | 2232 | |
| Crystal size | 0.31 x 0.13 x 0.08 $mm^3$ | |
| Theta range for data collection | 1.456 to 26.370°. | |
| Index ranges | -27<=h<=27, -19<=k<=11, -22<=l<=22 | |
| Reflections collected | 38417 | |
| Independent reflections | 6222 [R(int) = 0.0618] | |
| Completeness to theta = 25.242° | 100.0 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.5626 and 0.5095 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 6222 / 36 / 330 | |
| Goodness-of-fit on $F^2$ | 1.005 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0383, wR2 = 0.0908 | |
| R indices (all data) | R1 = 0.0760, wR2 = 0.1184 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 1.423 and -0.757 e.$Å^{-3}$ | |
| SQUEEZE | Found 78e/uc (likely two DCM) | |

**Table S2**. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for compound **2**_200K_sq. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| I(1) | 1844(1) | 2500 | 2500 | 29(1) |
| I(2) | 4999(1) | 2500 | 2500 | 34(1) |
| O(1) | 2015(1) | 3850(2) | 2779(2) | 46(1) |
| O(3) | 4851(2) | 1178(2) | 2133(2) | 55(1) |
| O(2) | 1011(2) | 3878(2) | 2773(2) | 55(1) |
| C(4) | 4034(2) | 2500 | 2500 | 23(1) |
| C(1) | 2808(2) | 2500 | 2500 | 24(1) |
| C(3) | 3742(2) | 2344(3) | 3166(2) | 26(1) |
| C(2) | 3096(2) | 2339(3) | 3164(2) | 28(1) |
| C(19) | 4070(2) | 2175(3) | 3874(2) | 32(1) |
| O(4) | 5856(2) | 1157(3) | 2173(3) | 82(1) |
| C(9) | 2757(2) | 2149(3) | 3856(2) | 35(1) |
| C(10) | 2531(2) | 1329(3) | 4010(3) | 52(1) |
| C(22) | 4592(2) | 1873(3) | 5270(2) | 48(1) |
| C(5) | 1496(2) | 4254(3) | 2861(3) | 42(1) |
| C(20) | 4180(3) | 1346(3) | 4124(3) | 57(2) |
| C(12) | 2119(3) | 1799(4) | 5173(3) | 59(2) |
| C(11) | 2213(3) | 1166(4) | 4664(3) | 64(2) |
| C(7) | 5378(3) | 797(4) | 2027(3) | 59(2) |
| C(24) | 4242(3) | 2856(4) | 4329(3) | 60(2) |
| C(23) | 4502(3) | 2696(3) | 5006(3) | 65(2) |
| C(21) | 4439(3) | 1195(3) | 4806(3) | 66(2) |
| C(25) | 4840(3) | 1708(4) | 6048(3) | 69(2) |
| C(14) | 2654(3) | 2799(4) | 4368(3) | 64(2) |
| C(6) | 1553(3) | 5198(3) | 3076(4) | 72(2) |
| C(13) | 2341(3) | 2614(4) | 5015(3) | 77(2) |
| C(15) | 1779(4) | 1622(5) | 5900(4) | 91(2) |
| C(27) | 5264(5) | 2392(5) | 6298(5) | 134(4) |
| C(8) | 5333(3) | -95(4) | 1678(4) | 90(2) |
| C(26) | 5079(5) | 815(5) | 6153(4) | 134(4) |
| C(16) | 1506(10) | 732(12) | 5923(10) | 131(7) |
| C(28) | 4273(5) | 1798(8) | 6589(4) | 165(5) |
| C(17) | 1303(10) | 2374(14) | 6009(13) | 191(12) |
| C(18) | 2295(10) | 1694(16) | 6537(6) | 152(8) |
| C(17A) | 1895(15) | 2150(20) | 6488(14) | 98(9) |
| C(18A) | 1870(20) | 710(30) | 6180(20) | 129(12) |
| C(16A) | 1094(12) | 1570(30) | 5743(13) | 116(12) |

**Table S3**. Bond lengths [Å] and angles [°] for compound **2**_200K_sq.

| | |
|---|---|
| I(1)-O(1)#1 | 2.152(3) |
| I(1)-O(1) | 2.152(3) |
| I(1)-C(1) | 2.115(5) |
| I(2)-O(3)#1 | 2.146(3) |
| I(2)-O(3) | 2.146(3) |
| I(2)-C(4) | 2.119(4) |
| O(1)-C(5) | 1.304(5) |
| O(3)-C(7) | 1.307(6) |
| O(2)-C(5) | 1.219(5) |
| C(4)-C(3) | 1.388(4) |
| C(4)-C(3)#1 | 1.388(4) |
| C(1)-C(2)#1 | 1.383(4) |
| C(1)-C(2) | 1.383(4) |
| C(3)-C(2) | 1.417(5) |
| C(3)-C(19) | 1.494(5) |
| C(2)-C(9) | 1.487(5) |
| C(19)-C(20) | 1.365(6) |
| C(19)-C(24) | 1.378(6) |
| O(4)-C(7) | 1.214(7) |
| C(9)-C(10) | 1.374(6) |
| C(9)-C(14) | 1.377(7) |
| C(10)-H(10) | 0.9500 |
| C(10)-C(11) | 1.398(6) |
| C(22)-C(23) | 1.357(7) |
| C(22)-C(21) | 1.373(7) |
| C(22)-C(25) | 1.533(6) |
| C(5)-C(6) | 1.496(7) |
| C(20)-H(20) | 0.9500 |
| C(20)-C(21) | 1.381(6) |
| C(12)-C(11) | 1.352(7) |
| C(12)-C(13) | 1.364(8) |
| C(12)-C(15) | 1.538(7) |
| C(11)-H(11) | 0.9500 |
| C(7)-C(8) | 1.503(8) |
| C(24)-H(24) | 0.9500 |
| C(24)-C(23) | 1.375(7) |
| C(23)-H(23) | 0.9500 |
| C(21)-H(21) | 0.9500 |
| C(25)-C(27) | 1.469(9) |
| C(25)-C(26) | 1.472(8) |
| C(25)-C(28) | 1.592(11) |
| C(14)-H(14) | 0.9500 |
| C(14)-C(13) | 1.388(7) |
| C(6)-H(6A) | 0.9800 |
| C(6)-H(6B) | 0.9800 |
| C(6)-H(6C) | 0.9800 |
| C(13)-H(13) | 0.9500 |
| C(15)-C(16) | 1.485(17) |
| C(15)-C(17) | 1.564(17) |
| C(15)-C(18) | 1.621(18) |
| C(15)-C(17A) | 1.36(3) |

| | |
|---|---|
| C(15)-C(18A) | 1.50(3) |
| C(15)-C(16A) | 1.53(3) |
| C(27)-H(27A) | 0.9800 |
| C(27)-H(27B) | 0.9800 |
| C(27)-H(27C) | 0.9800 |
| C(8)-H(8A) | 0.9800 |
| C(8)-H(8B) | 0.9800 |
| C(8)-H(8C) | 0.9800 |
| C(26)-H(26A) | 0.9800 |
| C(26)-H(26B) | 0.9800 |
| C(26)-H(26C) | 0.9800 |
| C(16)-H(16A) | 0.9800 |
| C(16)-H(16B) | 0.9800 |
| C(16)-H(16C) | 0.9800 |
| C(28)-H(28A) | 0.9800 |
| C(28)-H(28B) | 0.9800 |
| C(28)-H(28C) | 0.9800 |
| C(17)-H(17A) | 0.9800 |
| C(17)-H(17B) | 0.9800 |
| C(17)-H(17C) | 0.9800 |
| C(18)-H(18A) | 0.9800 |
| C(18)-H(18B) | 0.9800 |
| C(18)-H(18C) | 0.9800 |
| C(17A)-H(17D) | 0.9800 |
| C(17A)-H(17E) | 0.9800 |
| C(17A)-H(17F) | 0.9800 |
| C(18A)-H(18D) | 0.9800 |
| C(18A)-H(18E) | 0.9800 |
| C(18A)-H(18F) | 0.9800 |
| C(16A)-H(16D) | 0.9800 |
| C(16A)-H(16E) | 0.9800 |
| C(16A)-H(16F) | 0.9800 |

| | |
|---|---|
| O(1)-I(1)-O(1)#1 | 159.89(17) |
| C(1)-I(1)-O(1)#1 | 79.95(8) |
| C(1)-I(1)-O(1) | 79.95(8) |
| O(3)-I(2)-O(3)#1 | 162.65(18) |
| C(4)-I(2)-O(3)#1 | 81.32(9) |
| C(4)-I(2)-O(3) | 81.32(9) |
| C(5)-O(1)-I(1) | 109.0(3) |
| C(7)-O(3)-I(2) | 109.2(3) |
| C(3)#1-C(4)-I(2) | 117.5(2) |
| C(3)-C(4)-I(2) | 117.5(2) |
| C(3)-C(4)-C(3)#1 | 125.0(5) |
| C(2)-C(1)-I(1) | 117.3(2) |
| C(2)#1-C(1)-I(1) | 117.3(2) |
| C(2)#1-C(1)-C(2) | 125.4(5) |
| C(4)-C(3)-C(2) | 117.5(3) |
| C(4)-C(3)-C(19) | 123.7(4) |
| C(2)-C(3)-C(19) | 118.9(3) |
| C(1)-C(2)-C(3) | 117.3(4) |
| C(1)-C(2)-C(9) | 122.6(4) |
| C(3)-C(2)-C(9) | 120.0(4) |

| | |
|---|---|
| C(20)-C(19)-C(3) | 122.0(4) |
| C(20)-C(19)-C(24) | 116.7(4) |
| C(24)-C(19)-C(3) | 121.2(4) |
| C(10)-C(9)-C(2) | 122.0(4) |
| C(10)-C(9)-C(14) | 117.2(4) |
| C(14)-C(9)-C(2) | 120.8(4) |
| C(9)-C(10)-H(10) | 119.5 |
| C(9)-C(10)-C(11) | 121.0(5) |
| C(11)-C(10)-H(10) | 119.5 |
| C(23)-C(22)-C(21) | 116.4(4) |
| C(23)-C(22)-C(25) | 121.8(4) |
| C(21)-C(22)-C(25) | 121.8(5) |
| O(1)-C(5)-C(6) | 114.2(4) |
| O(2)-C(5)-O(1) | 121.9(4) |
| O(2)-C(5)-C(6) | 123.9(4) |
| C(19)-C(20)-H(20) | 119.1 |
| C(19)-C(20)-C(21) | 121.7(4) |
| C(21)-C(20)-H(20) | 119.1 |
| C(11)-C(12)-C(13) | 116.9(5) |
| C(11)-C(12)-C(15) | 122.3(6) |
| C(13)-C(12)-C(15) | 120.8(5) |
| C(10)-C(11)-H(11) | 119.0 |
| C(12)-C(11)-C(10) | 121.9(5) |
| C(12)-C(11)-H(11) | 119.0 |
| O(3)-C(7)-C(8) | 113.9(5) |
| O(4)-C(7)-O(3) | 122.1(5) |
| O(4)-C(7)-C(8) | 123.9(5) |
| C(19)-C(24)-H(24) | 119.5 |
| C(23)-C(24)-C(19) | 121.0(5) |
| C(23)-C(24)-H(24) | 119.5 |
| C(22)-C(23)-C(24) | 122.6(5) |
| C(22)-C(23)-H(23) | 118.7 |
| C(24)-C(23)-H(23) | 118.7 |
| C(22)-C(21)-C(20) | 121.5(5) |
| C(22)-C(21)-H(21) | 119.2 |
| C(20)-C(21)-H(21) | 119.2 |
| C(22)-C(25)-C(28) | 105.9(5) |
| C(27)-C(25)-C(22) | 113.2(5) |
| C(27)-C(25)-C(26) | 113.0(6) |
| C(27)-C(25)-C(28) | 104.2(7) |
| C(26)-C(25)-C(22) | 113.5(5) |
| C(26)-C(25)-C(28) | 106.2(7) |
| C(9)-C(14)-H(14) | 119.8 |
| C(9)-C(14)-C(13) | 120.4(5) |
| C(13)-C(14)-H(14) | 119.8 |
| C(5)-C(6)-H(6A) | 109.5 |
| C(5)-C(6)-H(6B) | 109.5 |
| C(5)-C(6)-H(6C) | 109.5 |
| H(6A)-C(6)-H(6B) | 109.5 |
| H(6A)-C(6)-H(6C) | 109.5 |
| H(6B)-C(6)-H(6C) | 109.5 |
| C(12)-C(13)-C(14) | 122.6(5) |
| C(12)-C(13)-H(13) | 118.7 |

| | |
|---|---|
| C(14)-C(13)-H(13) | 118.7 |
| C(12)-C(15)-C(17) | 107.8(8) |
| C(12)-C(15)-C(18) | 105.1(7) |
| C(16)-C(15)-C(12) | 112.4(9) |
| C(16)-C(15)-C(17) | 113.3(12) |
| C(16)-C(15)-C(18) | 108.9(11) |
| C(17)-C(15)-C(18) | 109.1(13) |
| C(17A)-C(15)-C(12) | 118.4(12) |
| C(17A)-C(15)-C(18A) | 105(2) |
| C(17A)-C(15)-C(16A) | 111.1(16) |
| C(18A)-C(15)-C(12) | 112.9(17) |
| C(18A)-C(15)-C(16A) | 98(2) |
| C(16A)-C(15)-C(12) | 109.1(10) |
| C(25)-C(27)-H(27A) | 109.5 |
| C(25)-C(27)-H(27B) | 109.5 |
| C(25)-C(27)-H(27C) | 109.5 |
| H(27A)-C(27)-H(27B) | 109.5 |
| H(27A)-C(27)-H(27C) | 109.5 |
| H(27B)-C(27)-H(27C) | 109.5 |
| C(7)-C(8)-H(8A) | 109.5 |
| C(7)-C(8)-H(8B) | 109.5 |
| C(7)-C(8)-H(8C) | 109.5 |
| H(8A)-C(8)-H(8B) | 109.5 |
| H(8A)-C(8)-H(8C) | 109.5 |
| H(8B)-C(8)-H(8C) | 109.5 |
| C(25)-C(26)-H(26A) | 109.5 |
| C(25)-C(26)-H(26B) | 109.5 |
| C(25)-C(26)-H(26C) | 109.5 |
| H(26A)-C(26)-H(26B) | 109.5 |
| H(26A)-C(26)-H(26C) | 109.5 |
| H(26B)-C(26)-H(26C) | 109.5 |
| C(15)-C(16)-H(16A) | 109.5 |
| C(15)-C(16)-H(16B) | 109.5 |
| C(15)-C(16)-H(16C) | 109.5 |
| H(16A)-C(16)-H(16B) | 109.5 |
| H(16A)-C(16)-H(16C) | 109.5 |
| H(16B)-C(16)-H(16C) | 109.5 |
| C(25)-C(28)-H(28A) | 109.5 |
| C(25)-C(28)-H(28B) | 109.5 |
| C(25)-C(28)-H(28C) | 109.5 |
| H(28A)-C(28)-H(28B) | 109.5 |
| H(28A)-C(28)-H(28C) | 109.5 |
| H(28B)-C(28)-H(28C) | 109.5 |
| C(15)-C(17)-H(17A) | 109.5 |
| C(15)-C(17)-H(17B) | 109.5 |
| C(15)-C(17)-H(17C) | 109.5 |
| H(17A)-C(17)-H(17B) | 109.5 |
| H(17A)-C(17)-H(17C) | 109.5 |
| H(17B)-C(17)-H(17C) | 109.5 |
| C(15)-C(18)-H(18A) | 109.5 |
| C(15)-C(18)-H(18B) | 109.5 |
| C(15)-C(18)-H(18C) | 109.5 |
| H(18A)-C(18)-H(18B) | 109.5 |

| | |
|---|---|
| H(18A)-C(18)-H(18C) | 109.5 |
| H(18B)-C(18)-H(18C) | 109.5 |
| C(15)-C(17A)-H(17D) | 109.5 |
| C(15)-C(17A)-H(17E) | 109.5 |
| C(15)-C(17A)-H(17F) | 109.5 |
| H(17D)-C(17A)-H(17E) | 109.5 |
| H(17D)-C(17A)-H(17F) | 109.5 |
| H(17E)-C(17A)-H(17F) | 109.5 |
| C(15)-C(18A)-H(18D) | 109.5 |
| C(15)-C(18A)-H(18E) | 109.5 |
| C(15)-C(18A)-H(18F) | 109.5 |
| H(18D)-C(18A)-H(18E) | 109.5 |
| H(18D)-C(18A)-H(18F) | 109.5 |
| H(18E)-C(18A)-H(18F) | 109.5 |
| C(15)-C(16A)-H(16D) | 109.5 |
| C(15)-C(16A)-H(16E) | 109.5 |
| C(15)-C(16A)-H(16F) | 109.5 |
| H(16D)-C(16A)-H(16E) | 109.5 |
| H(16D)-C(16A)-H(16F) | 109.5 |
| H(16E)-C(16A)-H(16F) | 109.5 |

Symmetry transformations used to generate equivalent atoms:
#1 x,-y+1/2,-z+1/2

**Table S4**. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for compound **2**_200K_sq. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| I(1) | 20(1) | 27(1) | 40(1) | -3(1) | 0 | 0 |
| I(2) | 23(1) | 42(1) | 39(1) | 0(1) | 0 | 0 |
| O(1) | 33(2) | 31(2) | 74(2) | -10(2) | -2(2) | -1(1) |
| O(3) | 43(2) | 46(2) | 76(2) | -12(2) | 4(2) | -2(2) |
| O(2) | 33(2) | 40(2) | 92(3) | -10(2) | -5(2) | 1(2) |
| C(4) | 14(2) | 25(3) | 29(2) | -2(3) | 0 | 0 |
| C(1) | 17(2) | 24(3) | 30(2) | 2(3) | 0 | 0 |
| C(3) | 25(2) | 27(3) | 27(2) | -1(2) | -2(2) | 2(2) |
| C(2) | 29(2) | 28(3) | 26(2) | -1(2) | 4(2) | 0(2) |
| C(19) | 34(2) | 34(2) | 26(2) | 3(2) | -2(2) | 0(2) |
| O(4) | 43(2) | 78(3) | 125(4) | -18(3) | 2(2) | 7(2) |
| C(9) | 35(2) | 42(3) | 28(2) | 2(2) | 7(2) | -2(2) |
| C(10) | 68(4) | 35(3) | 51(3) | 3(2) | 24(3) | 3(3) |
| C(22) | 60(3) | 48(3) | 36(2) | -2(2) | -14(2) | 3(3) |
| C(5) | 38(3) | 33(3) | 55(3) | -2(2) | -2(2) | 2(2) |
| C(20) | 93(4) | 34(3) | 44(3) | -10(2) | -32(3) | 8(3) |
| C(12) | 59(3) | 68(4) | 50(3) | 3(3) | 23(3) | -5(3) |
| C(11) | 78(4) | 47(3) | 66(4) | 12(3) | 34(3) | -4(3) |
| C(7) | 54(4) | 55(4) | 68(4) | -3(3) | 6(3) | 13(3) |
| C(24) | 97(5) | 33(3) | 49(3) | 2(2) | -28(3) | -4(3) |
| C(23) | 101(5) | 43(4) | 50(3) | -9(2) | -36(3) | 1(3) |
| C(21) | 111(5) | 33(3) | 55(3) | -4(3) | -39(3) | 7(3) |
| C(25) | 109(5) | 53(4) | 45(3) | -8(3) | -36(3) | 4(4) |
| C(14) | 98(5) | 46(3) | 46(3) | -11(2) | 29(3) | -19(3) |
| C(6) | 50(3) | 38(3) | 129(6) | -19(3) | 4(4) | 4(3) |
| C(13) | 99(5) | 74(5) | 58(3) | -28(3) | 39(3) | -16(4) |
| C(15) | 99(5) | 109(5) | 64(4) | 4(4) | 49(3) | -12(4) |
| C(27) | 202(10) | 97(6) | 103(6) | 11(5) | -110(7) | -17(6) |
| C(8) | 94(6) | 58(4) | 119(6) | -20(4) | 22(5) | 7(4) |
| C(26) | 244(11) | 89(6) | 70(5) | -16(4) | -97(6) | 64(6) |
| C(16) | 169(19) | 138(8) | 86(13) | 3(9) | 67(11) | -60(10) |
| C(28) | 216(12) | 238(13) | 40(4) | 0(6) | -7(6) | 55(10) |
| C(17) | 186(17) | 175(13) | 210(20) | 43(16) | 172(16) | 55(14) |
| C(18) | 181(13) | 240(20) | 41(5) | -1(9) | 34(6) | -65(12) |
| C(17A) | 96(18) | 140(16) | 57(9) | -3(10) | 55(10) | -24(14) |
| C(18A) | 190(30) | 126(9) | 70(20) | 27(11) | 60(20) | 8(14) |
| C(16A) | 100(7) | 190(30) | 60(12) | 9(16) | 46(8) | -31(12) |

**Table S5**. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for compound **2**_200K_sq.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(10) | 2591 | 865 | 3667 | 62 |
| H(20) | 4076 | 860 | 3821 | 68 |
| H(11) | 2058 | 593 | 4752 | 76 |
| H(24) | 4180 | 3444 | 4173 | 72 |
| H(23) | 4624 | 3181 | 5300 | 78 |
| H(21) | 4514 | 608 | 4959 | 80 |
| H(14) | 2797 | 3378 | 4279 | 76 |
| H(6A) | 1604 | 5243 | 3611 | 108 |
| H(6B) | 1185 | 5515 | 2927 | 108 |
| H(6C) | 1908 | 5456 | 2830 | 108 |
| H(13) | 2279 | 3073 | 5362 | 92 |
| H(27A) | 5634 | 2376 | 5995 | 201 |
| H(27B) | 5372 | 2288 | 6815 | 201 |
| H(27C) | 5070 | 2969 | 6250 | 201 |
| H(8A) | 5002 | -427 | 1911 | 135 |
| H(8B) | 5718 | -410 | 1745 | 135 |
| H(8C) | 5249 | -31 | 1150 | 135 |
| H(26A) | 4768 | 386 | 6009 | 201 |
| H(26B) | 5185 | 729 | 6673 | 201 |
| H(26C) | 5443 | 734 | 5848 | 201 |
| H(16A) | 1221 | 663 | 5511 | 196 |
| H(16B) | 1287 | 654 | 6390 | 196 |
| H(16C) | 1828 | 290 | 5884 | 196 |
| H(28A) | 4088 | 2380 | 6529 | 247 |
| H(28B) | 4409 | 1726 | 7100 | 247 |
| H(28C) | 3972 | 1345 | 6471 | 247 |
| H(17A) | 1516 | 2922 | 6129 | 286 |
| H(17B) | 1027 | 2220 | 6413 | 286 |
| H(17C) | 1069 | 2453 | 5554 | 286 |
| H(18A) | 2610 | 1251 | 6450 | 228 |
| H(18B) | 2107 | 1595 | 7020 | 228 |
| H(18C) | 2478 | 2280 | 6525 | 228 |
| H(17D) | 2330 | 2130 | 6607 | 146 |
| H(17E) | 1658 | 1953 | 6914 | 146 |
| H(17F) | 1781 | 2758 | 6366 | 146 |
| H(18D) | 1760 | 288 | 5789 | 193 |
| H(18E) | 1605 | 609 | 6608 | 193 |
| H(18F) | 2294 | 623 | 6319 | 193 |
| H(16D) | 949 | 2138 | 5562 | 173 |
| H(16E) | 877 | 1417 | 6198 | 173 |
| H(16F) | 1017 | 1117 | 5370 | 173 |

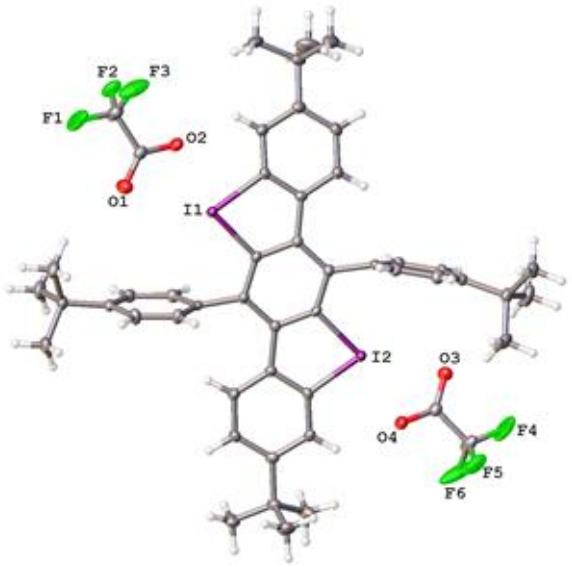



**Figure S6.** Structural diagram of compound **3**.

**Table S6**. Crystal data and structure refinement for compound **3**_0m_a.

| | | |
|---|---|---|
| Identification code | compound **3** | |
| Empirical formula | $C_{50}$ $H_{50}$ $F_6$ $I_2$ $O_4$ | |
| Formula weight | 1082.70 | |
| Temperature | 100.0 K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit cell dimensions | a = 12.7903(7) Å | □= 67.9580(10)°. |
| | b = 14.1970(6) Å | □= 74.535(2)°. |
| | c = 14.4995(8) Å | □ = 80.5310(10)°. |
| Volume | 2345.9(2) Å$^3$ | |
| Z | 2 | |
| Density (calculated) | 1.533 Mg/m$^3$ | |
| Absorption coefficient | 1.407 mm$^{-1}$ | |
| F(000) | 1084 | |
| Crystal size | 0.26 x 0.12 x 0.08 mm$^3$ | |
| Theta range for data collection | 2.186 to 26.392°. | |
| Index ranges | -15<=h<=15, -17<=k<=17, -18<=l<=18 | |
| Reflections collected | 40984 | |
| Independent reflections | 9576 [R(int) = 0.0308] | |
| Completeness to theta = 25.242° | 99.7 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7454 and 0.6671 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 9576 / 0 / 571 | |
| Goodness-of-fit on $F^2$ | 1.031 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0233, wR2 = 0.0600 | |
| R indices (all data) | R1 = 0.0284, wR2 = 0.0634 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 1.065 and -0.787 e.Å$^{-3}$ | |

**TableS7**. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for compound **3** _0m_a. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| I(1) | 4758(1) | 5668(1) | 3527(1) | 16(1) |
| I(2) | 10004(1) | 4265(1) | 1581(1) | 17(1) |
| F(2) | 880(1) | 7246(1) | 4277(1) | 34(1) |
| F(5) | 14010(1) | 3134(1) | 861(1) | 42(1) |
| O(4) | 11794(1) | 3307(1) | 952(1) | 28(1) |
| O(2) | 3072(1) | 6679(1) | 4154(1) | 28(1) |
| F(1) | 520(1) | 6035(2) | 5719(2) | 73(1) |
| O(3) | 12145(1) | 4916(1) | -58(1) | 29(1) |
| F(3) | 1381(2) | 7267(2) | 5552(2) | 62(1) |
| O(1) | 2451(2) | 5146(1) | 5132(2) | 38(1) |
| C(4) | 8401(2) | 4715(2) | 2179(2) | 16(1) |
| C(1) | 6350(2) | 5207(2) | 2903(2) | 16(1) |
| C(6) | 6595(2) | 4215(2) | 2898(2) | 17(1) |
| C(3) | 8163(2) | 5699(2) | 2194(2) | 17(1) |
| C(37) | 3994(2) | 3152(2) | 3078(2) | 20(1) |
| F(6) | 13726(2) | 2984(2) | -436(2) | 85(1) |
| C(27) | 9293(2) | 2895(2) | 2000(2) | 17(1) |
| C(35) | 4384(2) | 2519(2) | 4733(2) | 23(1) |
| C(5) | 7681(2) | 3959(2) | 2493(2) | 16(1) |
| C(7) | 5450(2) | 7078(2) | 2934(2) | 17(1) |
| C(2) | 7071(2) | 5973(2) | 2550(2) | 16(1) |
| C(36) | 3668(2) | 2608(2) | 4119(2) | 19(1) |
| C(20) | 11283(2) | 6894(2) | 1329(2) | 19(1) |
| C(33) | 5655(2) | 3554(2) | 3301(2) | 16(1) |
| C(34) | 5356(2) | 2983(2) | 4341(2) | 21(1) |
| C(17) | 9131(2) | 6313(2) | 1883(2) | 16(1) |
| C(19) | 10701(2) | 6577(2) | 2350(2) | 22(1) |
| C(38) | 4971(2) | 3621(2) | 2673(2) | 20(1) |
| C(22) | 9665(2) | 6706(2) | 855(2) | 19(1) |
| C(32) | 8165(2) | 2977(2) | 2382(2) | 16(1) |
| C(47) | 2369(2) | 6070(2) | 4770(2) | 22(1) |

| | | | | |
|---|---|---|---|---|
| C(21) | 10726(2) | 6990(2) | 587(2) | 20(1) |
| C(12) | 4834(2) | 7984(2) | 2894(2) | 19(1) |
| C(49) | 12392(2) | 4009(2) | 333(2) | 20(1) |
| C(30) | 8207(2) | 1236(2) | 2458(2) | 20(1) |
| C(18) | 9648(2) | 6288(2) | 2628(2) | 20(1) |
| F(4) | 14206(2) | 4373(2) | -542(2) | 122(1) |
| C(23) | 12509(2) | 7009(2) | 1072(2) | 23(1) |
| C(8) | 6568(2) | 6988(2) | 2541(2) | 17(1) |
| C(48) | 1272(2) | 6640(2) | 5083(2) | 30(1) |
| C(46) | 1915(2) | 2663(2) | 5370(2) | 30(1) |
| C(28) | 9883(2) | 2034(2) | 1860(2) | 18(1) |
| C(31) | 7633(2) | 2104(2) | 2612(2) | 19(1) |
| C(29) | 9330(2) | 1176(2) | 2080(2) | 19(1) |
| C(10) | 6482(2) | 8821(2) | 2043(2) | 24(1) |
| C(43) | 2564(2) | 2151(2) | 4599(2) | 22(1) |
| C(9) | 7081(2) | 7903(2) | 2097(2) | 21(1) |
| C(11) | 5356(2) | 8888(2) | 2425(2) | 22(1) |
| C(50) | 13591(2) | 3629(2) | 55(2) | 32(1) |
| C(39) | 9982(2) | 217(2) | 1921(2) | 23(1) |
| C(45) | 1895(2) | 2329(2) | 3806(2) | 31(1) |
| C(24) | 12762(2) | 7740(2) | 1528(2) | 29(1) |
| C(42) | 9246(2) | -526(2) | 1913(2) | 33(1) |
| C(44) | 2741(2) | 999(2) | 5157(2) | 32(1) |
| C(26) | 12989(2) | 7375(2) | -74(2) | 37(1) |
| C(15) | 5218(2) | 10561(2) | 2687(3) | 42(1) |
| C(25) | 13054(2) | 5940(2) | 1559(2) | 31(1) |
| C(13) | 4719(2) | 9926(2) | 2285(2) | 29(1) |
| C(41) | 10812(2) | 510(2) | 892(2) | 35(1) |
| C(40) | 10570(2) | -311(2) | 2794(2) | 33(1) |
| C(16) | 3525(2) | 9823(2) | 2831(3) | 48(1) |
| C(14) | 4781(3) | 10481(2) | 1130(3) | 55(1) |

**Table S8**. Bond lengths [Å] and angles [°] for compound **3**_0m_a.

| | |
|---|---|
| I(1)-C(1) | 2.101(2) |
| I(1)-C(7) | 2.101(2) |
| I(2)-C(4) | 2.098(2) |
| I(2)-C(27) | 2.093(2) |
| F(2)-C(48) | 1.332(3) |
| F(5)-C(50) | 1.319(3) |
| O(4)-C(49) | 1.264(3) |
| O(2)-C(47) | 1.266(3) |
| F(1)-C(48) | 1.310(3) |
| O(3)-C(49) | 1.222(3) |
| F(3)-C(48) | 1.349(3) |
| O(1)-C(47) | 1.214(3) |
| C(4)-C(3) | 1.388(3) |
| C(4)-C(5) | 1.394(3) |
| C(1)-C(6) | 1.393(3) |
| C(1)-C(2) | 1.399(3) |
| C(6)-C(5) | 1.402(3) |
| C(6)-C(33) | 1.501(3) |
| C(3)-C(2) | 1.399(3) |
| C(3)-C(17) | 1.502(3) |
| C(37)-H(37) | 0.9500 |
| C(37)-C(36) | 1.395(3) |
| C(37)-C(38) | 1.392(3) |
| F(6)-C(50) | 1.322(3) |
| C(27)-C(32) | 1.403(3) |
| C(27)-C(28) | 1.381(3) |
| C(35)-H(35) | 0.9500 |
| C(35)-C(36) | 1.400(3) |
| C(35)-C(34) | 1.383(3) |
| C(5)-C(32) | 1.477(3) |
| C(7)-C(12) | 1.383(3) |
| C(7)-C(8) | 1.394(3) |
| C(2)-C(8) | 1.475(3) |
| C(36)-C(43) | 1.529(3) |

| | |
|---|---|
| C(20)-C(19) | 1.405(3) |
| C(20)-C(21) | 1.396(3) |
| C(20)-C(23) | 1.533(3) |
| C(33)-C(34) | 1.397(3) |
| C(33)-C(38) | 1.392(3) |
| C(34)-H(34) | 0.9500 |
| C(17)-C(22) | 1.399(3) |
| C(17)-C(18) | 1.397(3) |
| C(19)-H(19) | 0.9500 |
| C(19)-C(18) | 1.383(3) |
| C(38)-H(38) | 0.9500 |
| C(22)-H(22) | 0.9500 |
| C(22)-C(21) | 1.391(3) |
| C(32)-C(31) | 1.398(3) |
| C(47)-C(48) | 1.547(3) |
| C(21)-H(21) | 0.9500 |
| C(12)-H(12) | 0.9500 |
| C(12)-C(11) | 1.393(3) |
| C(49)-C(50) | 1.537(3) |
| C(30)-H(30) | 0.9500 |
| C(30)-C(31) | 1.389(3) |
| C(30)-C(29) | 1.395(3) |
| C(18)-H(18) | 0.9500 |
| F(4)-C(50) | 1.308(3) |
| C(23)-C(24) | 1.534(3) |
| C(23)-C(26) | 1.524(3) |
| C(23)-C(25) | 1.549(3) |
| C(8)-C(9) | 1.400(3) |
| C(46)-H(46A) | 0.9800 |
| C(46)-H(46B) | 0.9800 |
| C(46)-H(46C) | 0.9800 |
| C(46)-C(43) | 1.543(3) |
| C(28)-H(28) | 0.9500 |
| C(28)-C(29) | 1.399(3) |
| C(31)-H(31) | 0.9500 |
| C(29)-C(39) | 1.537(3) |

| | |
|---|---|
| C(10)-H(10) | 0.9500 |
| C(10)-C(9) | 1.385(3) |
| C(10)-C(11) | 1.400(3) |
| C(43)-C(45) | 1.534(3) |
| C(43)-C(44) | 1.537(3) |
| C(9)-H(9) | 0.9500 |
| C(11)-C(13) | 1.531(3) |
| C(39)-C(42) | 1.531(3) |
| C(39)-C(41) | 1.536(3) |
| C(39)-C(40) | 1.529(3) |
| C(45)-H(45A) | 0.9800 |
| C(45)-H(45B) | 0.9800 |
| C(45)-H(45C) | 0.9800 |
| C(24)-H(24A) | 0.9800 |
| C(24)-H(24B) | 0.9800 |
| C(24)-H(24C) | 0.9800 |
| C(42)-H(42A) | 0.9800 |
| C(42)-H(42B) | 0.9800 |
| C(42)-H(42C) | 0.9800 |
| C(44)-H(44A) | 0.9800 |
| C(44)-H(44B) | 0.9800 |
| C(44)-H(44C) | 0.9800 |
| C(26)-H(26A) | 0.9800 |
| C(26)-H(26B) | 0.9800 |
| C(26)-H(26C) | 0.9800 |
| C(15)-H(15A) | 0.9800 |
| C(15)-H(15B) | 0.9800 |
| C(15)-H(15C) | 0.9800 |
| C(15)-C(13) | 1.530(3) |
| C(25)-H(25A) | 0.9800 |
| C(25)-H(25B) | 0.9800 |
| C(25)-H(25C) | 0.9800 |
| C(13)-C(16) | 1.524(4) |
| C(13)-C(14) | 1.545(4) |
| C(41)-H(41A) | 0.9800 |
| C(41)-H(41B) | 0.9800 |

| | |
|---|---|
| C(41)-H(41C) | 0.9800 |
| C(40)-H(40A) | 0.9800 |
| C(40)-H(40B) | 0.9800 |
| C(40)-H(40C) | 0.9800 |
| C(16)-H(16A) | 0.9800 |
| C(16)-H(16B) | 0.9800 |
| C(16)-H(16C) | 0.9800 |
| C(14)-H(14A) | 0.9800 |
| C(14)-H(14B) | 0.9800 |
| C(14)-H(14C) | 0.9800 |

| | |
|---|---|
| C(1)-I(1)-C(7) | 80.94(8) |
| C(27)-I(2)-C(4) | 81.08(8) |
| C(3)-C(4)-I(2) | 118.96(15) |
| C(3)-C(4)-C(5) | 127.62(19) |
| C(5)-C(4)-I(2) | 113.39(15) |
| C(6)-C(1)-I(1) | 119.93(15) |
| C(6)-C(1)-C(2) | 127.04(19) |
| C(2)-C(1)-I(1) | 113.01(15) |
| C(1)-C(6)-C(5) | 116.48(19) |
| C(1)-C(6)-C(33) | 115.96(18) |
| C(5)-C(6)-C(33) | 127.53(19) |
| C(4)-C(3)-C(2) | 116.39(19) |
| C(4)-C(3)-C(17) | 115.16(18) |
| C(2)-C(3)-C(17) | 128.34(19) |
| C(36)-C(37)-H(37) | 119.3 |
| C(38)-C(37)-H(37) | 119.3 |
| C(38)-C(37)-C(36) | 121.4(2) |
| C(32)-C(27)-I(2) | 112.43(15) |
| C(28)-C(27)-I(2) | 122.45(16) |
| C(28)-C(27)-C(32) | 125.05(19) |
| C(36)-C(35)-H(35) | 119.0 |
| C(34)-C(35)-H(35) | 119.0 |
| C(34)-C(35)-C(36) | 121.9(2) |
| C(4)-C(5)-C(6) | 116.05(19) |
| C(4)-C(5)-C(32) | 115.78(18) |

| | |
|---|---|
| C(6)-C(5)-C(32) | 128.14(19) |
| C(12)-C(7)-I(1) | 122.55(15) |
| C(12)-C(7)-C(8) | 125.23(19) |
| C(8)-C(7)-I(1) | 112.11(15) |
| C(1)-C(2)-C(3) | 116.29(19) |
| C(1)-C(2)-C(8) | 115.47(18) |
| C(3)-C(2)-C(8) | 128.11(19) |
| C(37)-C(36)-C(35) | 117.18(19) |
| C(37)-C(36)-C(43) | 122.64(19) |
| C(35)-C(36)-C(43) | 120.16(19) |
| C(19)-C(20)-C(23) | 120.14(19) |
| C(21)-C(20)-C(19) | 117.2(2) |
| C(21)-C(20)-C(23) | 122.3(2) |
| C(34)-C(33)-C(6) | 120.67(19) |
| C(38)-C(33)-C(6) | 119.96(19) |
| C(38)-C(33)-C(34) | 118.67(19) |
| C(35)-C(34)-C(33) | 120.2(2) |
| C(35)-C(34)-H(34) | 119.9 |
| C(33)-C(34)-H(34) | 119.9 |
| C(22)-C(17)-C(3) | 120.30(19) |
| C(18)-C(17)-C(3) | 119.20(19) |
| C(18)-C(17)-C(22) | 118.81(19) |
| C(20)-C(19)-H(19) | 119.0 |
| C(18)-C(19)-C(20) | 121.9(2) |
| C(18)-C(19)-H(19) | 119.0 |
| C(37)-C(38)-H(38) | 119.7 |
| C(33)-C(38)-C(37) | 120.6(2) |
| C(33)-C(38)-H(38) | 119.7 |
| C(17)-C(22)-H(22) | 119.8 |
| C(21)-C(22)-C(17) | 120.3(2) |
| C(21)-C(22)-H(22) | 119.8 |
| C(27)-C(32)-C(5) | 117.14(18) |
| C(31)-C(32)-C(27) | 115.06(19) |
| C(31)-C(32)-C(5) | 127.80(19) |
| O(2)-C(47)-C(48) | 111.8(2) |
| O(1)-C(47)-O(2) | 129.4(2) |

| | |
|---|---|
| O(1)-C(47)-C(48) | 118.7(2) |
| C(20)-C(21)-H(21) | 119.3 |
| C(22)-C(21)-C(20) | 121.3(2) |
| C(22)-C(21)-H(21) | 119.3 |
| C(7)-C(12)-H(12) | 120.8 |
| C(7)-C(12)-C(11) | 118.4(2) |
| C(11)-C(12)-H(12) | 120.8 |
| O(4)-C(49)-C(50) | 113.1(2) |
| O(3)-C(49)-O(4) | 129.1(2) |
| O(3)-C(49)-C(50) | 117.8(2) |
| C(31)-C(30)-H(30) | 118.6 |
| C(31)-C(30)-C(29) | 122.7(2) |
| C(29)-C(30)-H(30) | 118.6 |
| C(17)-C(18)-H(18) | 120.0 |
| C(19)-C(18)-C(17) | 120.0(2) |
| C(19)-C(18)-H(18) | 120.0 |
| C(20)-C(23)-C(24) | 111.13(19) |
| C(20)-C(23)-C(25) | 106.94(18) |
| C(24)-C(23)-C(25) | 108.68(19) |
| C(26)-C(23)-C(20) | 112.29(19) |
| C(26)-C(23)-C(24) | 109.5(2) |
| C(26)-C(23)-C(25) | 108.2(2) |
| C(7)-C(8)-C(2) | 117.76(18) |
| C(7)-C(8)-C(9) | 115.45(19) |
| C(9)-C(8)-C(2) | 126.55(19) |
| F(2)-C(48)-F(3) | 104.8(2) |
| F(2)-C(48)-C(47) | 112.04(19) |
| F(1)-C(48)-F(2) | 108.3(2) |
| F(1)-C(48)-F(3) | 105.9(2) |
| F(1)-C(48)-C(47) | 113.7(2) |
| F(3)-C(48)-C(47) | 111.6(2) |
| H(46A)-C(46)-H(46B) | 109.5 |
| H(46A)-C(46)-H(46C) | 109.5 |
| H(46B)-C(46)-H(46C) | 109.5 |
| C(43)-C(46)-H(46A) | 109.5 |
| C(43)-C(46)-H(46B) | 109.5 |

| | |
|---|---|
| C(43)-C(46)-H(46C) | 109.5 |
| C(27)-C(28)-H(28) | 120.6 |
| C(27)-C(28)-C(29) | 118.8(2) |
| C(29)-C(28)-H(28) | 120.6 |
| C(32)-C(31)-H(31) | 119.5 |
| C(30)-C(31)-C(32) | 120.9(2) |
| C(30)-C(31)-H(31) | 119.5 |
| C(30)-C(29)-C(28) | 117.43(19) |
| C(30)-C(29)-C(39) | 123.50(19) |
| C(28)-C(29)-C(39) | 119.06(19) |
| C(9)-C(10)-H(10) | 118.6 |
| C(9)-C(10)-C(11) | 122.7(2) |
| C(11)-C(10)-H(10) | 118.6 |
| C(36)-C(43)-C(46) | 108.30(18) |
| C(36)-C(43)-C(45) | 112.47(19) |
| C(36)-C(43)-C(44) | 109.23(18) |
| C(45)-C(43)-C(46) | 108.13(19) |
| C(45)-C(43)-C(44) | 108.99(19) |
| C(44)-C(43)-C(46) | 109.7(2) |
| C(8)-C(9)-H(9) | 119.8 |
| C(10)-C(9)-C(8) | 120.5(2) |
| C(10)-C(9)-H(9) | 119.8 |
| C(12)-C(11)-C(10) | 117.7(2) |
| C(12)-C(11)-C(13) | 121.5(2) |
| C(10)-C(11)-C(13) | 120.8(2) |
| F(5)-C(50)-F(6) | 105.2(2) |
| F(5)-C(50)-C(49) | 113.08(19) |
| F(6)-C(50)-C(49) | 112.3(2) |
| F(4)-C(50)-F(5) | 107.4(3) |
| F(4)-C(50)-F(6) | 106.0(3) |
| F(4)-C(50)-C(49) | 112.2(2) |
| C(42)-C(39)-C(29) | 111.78(19) |
| C(42)-C(39)-C(41) | 107.6(2) |
| C(41)-C(39)-C(29) | 110.10(18) |
| C(40)-C(39)-C(29) | 108.23(19) |
| C(40)-C(39)-C(42) | 109.1(2) |

| | |
|---|---|
| C(40)-C(39)-C(41) | 110.1(2) |
| C(43)-C(45)-H(45A) | 109.5 |
| C(43)-C(45)-H(45B) | 109.5 |
| C(43)-C(45)-H(45C) | 109.5 |
| H(45A)-C(45)-H(45B) | 109.5 |
| H(45A)-C(45)-H(45C) | 109.5 |
| H(45B)-C(45)-H(45C) | 109.5 |
| C(23)-C(24)-H(24A) | 109.5 |
| C(23)-C(24)-H(24B) | 109.5 |
| C(23)-C(24)-H(24C) | 109.5 |
| H(24A)-C(24)-H(24B) | 109.5 |
| H(24A)-C(24)-H(24C) | 109.5 |
| H(24B)-C(24)-H(24C) | 109.5 |
| C(39)-C(42)-H(42A) | 109.5 |
| C(39)-C(42)-H(42B) | 109.5 |
| C(39)-C(42)-H(42C) | 109.5 |
| H(42A)-C(42)-H(42B) | 109.5 |
| H(42A)-C(42)-H(42C) | 109.5 |
| H(42B)-C(42)-H(42C) | 109.5 |
| C(43)-C(44)-H(44A) | 109.5 |
| C(43)-C(44)-H(44B) | 109.5 |
| C(43)-C(44)-H(44C) | 109.5 |
| H(44A)-C(44)-H(44B) | 109.5 |
| H(44A)-C(44)-H(44C) | 109.5 |
| H(44B)-C(44)-H(44C) | 109.5 |
| C(23)-C(26)-H(26A) | 109.5 |
| C(23)-C(26)-H(26B) | 109.5 |
| C(23)-C(26)-H(26C) | 109.5 |
| H(26A)-C(26)-H(26B) | 109.5 |
| H(26A)-C(26)-H(26C) | 109.5 |
| H(26B)-C(26)-H(26C) | 109.5 |
| H(15A)-C(15)-H(15B) | 109.5 |
| H(15A)-C(15)-H(15C) | 109.5 |
| H(15B)-C(15)-H(15C) | 109.5 |
| C(13)-C(15)-H(15A) | 109.5 |
| C(13)-C(15)-H(15B) | 109.5 |

| | |
|---|---|
| C(13)-C(15)-H(15C) | 109.5 |
| C(23)-C(25)-H(25A) | 109.5 |
| C(23)-C(25)-H(25B) | 109.5 |
| C(23)-C(25)-H(25C) | 109.5 |
| H(25A)-C(25)-H(25B) | 109.5 |
| H(25A)-C(25)-H(25C) | 109.5 |
| H(25B)-C(25)-H(25C) | 109.5 |
| C(11)-C(13)-C(14) | 107.8(2) |
| C(15)-C(13)-C(11) | 110.3(2) |
| C(15)-C(13)-C(14) | 109.4(2) |
| C(16)-C(13)-C(11) | 112.0(2) |
| C(16)-C(13)-C(15) | 108.9(2) |
| C(16)-C(13)-C(14) | 108.3(2) |
| C(39)-C(41)-H(41A) | 109.5 |
| C(39)-C(41)-H(41B) | 109.5 |
| C(39)-C(41)-H(41C) | 109.5 |
| H(41A)-C(41)-H(41B) | 109.5 |
| H(41A)-C(41)-H(41C) | 109.5 |
| H(41B)-C(41)-H(41C) | 109.5 |
| C(39)-C(40)-H(40A) | 109.5 |
| C(39)-C(40)-H(40B) | 109.5 |
| C(39)-C(40)-H(40C) | 109.5 |
| H(40A)-C(40)-H(40B) | 109.5 |
| H(40A)-C(40)-H(40C) | 109.5 |
| H(40B)-C(40)-H(40C) | 109.5 |
| C(13)-C(16)-H(16A) | 109.5 |
| C(13)-C(16)-H(16B) | 109.5 |
| C(13)-C(16)-H(16C) | 109.5 |
| H(16A)-C(16)-H(16B) | 109.5 |
| H(16A)-C(16)-H(16C) | 109.5 |
| H(16B)-C(16)-H(16C) | 109.5 |
| C(13)-C(14)-H(14A) | 109.5 |
| C(13)-C(14)-H(14B) | 109.5 |
| C(13)-C(14)-H(14C) | 109.5 |
| H(14A)-C(14)-H(14B) | 109.5 |
| H(14A)-C(14)-H(14C) | 109.5 |

| | |
|---|---|
| H(14B)-C(14)-H(14C) | 109.5 |

Symmetry transformations used to generate equivalent atoms:

**Table S9**. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for compound **3**_0m_a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| I(1) | 12(1) | 15(1) | 19(1) | -5(1) | -2(1) | 0(1) |
| I(2) | 12(1) | 15(1) | 22(1) | -6(1) | 0(1) | -1(1) |
| F(2) | 25(1) | 45(1) | 26(1) | -10(1) | -10(1) | 12(1) |
| F(5) | 27(1) | 66(1) | 33(1) | -20(1) | -15(1) | 14(1) |
| O(4) | 18(1) | 22(1) | 37(1) | -8(1) | 2(1) | -2(1) |
| O(2) | 19(1) | 23(1) | 35(1) | -9(1) | 2(1) | 1(1) |
| F(1) | 28(1) | 58(1) | 76(1) | 15(1) | 20(1) | 7(1) |
| O(3) | 25(1) | 21(1) | 32(1) | -4(1) | -3(1) | 0(1) |
| F(3) | 58(1) | 89(1) | 60(1) | -58(1) | -31(1) | 41(1) |
| O(1) | 32(1) | 23(1) | 48(1) | -8(1) | 3(1) | -2(1) |
| C(4) | 11(1) | 18(1) | 18(1) | -7(1) | -1(1) | 2(1) |
| C(1) | 12(1) | 17(1) | 16(1) | -5(1) | -2(1) | 1(1) |
| C(6) | 14(1) | 17(1) | 16(1) | -4(1) | -3(1) | -1(1) |
| C(3) | 16(1) | 18(1) | 16(1) | -5(1) | -3(1) | -1(1) |
| C(37) | 18(1) | 22(1) | 23(1) | -8(1) | -6(1) | -1(1) |
| F(6) | 68(1) | 145(2) | 67(1) | -82(2) | -42(1) | 73(1) |
| C(27) | 18(1) | 14(1) | 16(1) | -3(1) | -3(1) | -3(1) |
| C(35) | 22(1) | 25(1) | 18(1) | -2(1) | -2(1) | -8(1) |
| C(5) | 15(1) | 16(1) | 14(1) | -4(1) | -3(1) | -1(1) |
| C(7) | 17(1) | 15(1) | 18(1) | -5(1) | -4(1) | -4(1) |
| C(2) | 16(1) | 16(1) | 15(1) | -5(1) | -3(1) | 0(1) |
| C(36) | 16(1) | 18(1) | 23(1) | -9(1) | -2(1) | -2(1) |
| C(20) | 17(1) | 17(1) | 22(1) | -7(1) | -3(1) | -2(1) |
| C(33) | 12(1) | 14(1) | 21(1) | -7(1) | -1(1) | 0(1) |
| C(34) | 17(1) | 25(1) | 20(1) | -5(1) | -6(1) | -3(1) |
| C(17) | 13(1) | 13(1) | 22(1) | -6(1) | -2(1) | 0(1) |
| C(19) | 20(1) | 28(1) | 23(1) | -12(1) | -4(1) | -2(1) |
| C(38) | 21(1) | 19(1) | 18(1) | -5(1) | -3(1) | -3(1) |
| C(22) | 19(1) | 19(1) | 19(1) | -3(1) | -7(1) | -3(1) |
| C(32) | 16(1) | 15(1) | 16(1) | -4(1) | -3(1) | 0(1) |
| C(47) | 18(1) | 27(1) | 21(1) | -9(1) | -4(1) | 1(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(21) | 18(1) | 20(1) | 20(1) | -4(1) | -1(1) | -5(1) |
| C(12) | 15(1) | 21(1) | 22(1) | -9(1) | -6(1) | 1(1) |
| C(49) | 18(1) | 24(1) | 18(1) | -9(1) | -2(1) | -1(1) |
| C(30) | 20(1) | 14(1) | 25(1) | -4(1) | -4(1) | -2(1) |
| C(18) | 20(1) | 21(1) | 19(1) | -10(1) | 0(1) | -2(1) |
| F(4) | 23(1) | 68(2) | 163(3) | 50(2) | 26(1) | 3(1) |
| C(23) | 16(1) | 28(1) | 25(1) | -10(1) | -3(1) | -4(1) |
| C(8) | 18(1) | 16(1) | 17(1) | -7(1) | -6(1) | 2(1) |
| C(48) | 23(1) | 35(1) | 21(1) | -4(1) | -1(1) | 5(1) |
| C(46) | 18(1) | 39(2) | 33(1) | -18(1) | 3(1) | -6(1) |
| C(28) | 15(1) | 18(1) | 18(1) | -3(1) | -3(1) | 1(1) |
| C(31) | 15(1) | 19(1) | 21(1) | -6(1) | -1(1) | -1(1) |
| C(29) | 21(1) | 17(1) | 16(1) | -4(1) | -3(1) | 2(1) |
| C(10) | 23(1) | 17(1) | 31(1) | -8(1) | -5(1) | -4(1) |
| C(43) | 16(1) | 24(1) | 26(1) | -9(1) | -1(1) | -5(1) |
| C(9) | 17(1) | 19(1) | 28(1) | -9(1) | -2(1) | -3(1) |
| C(11) | 21(1) | 20(1) | 28(1) | -11(1) | -9(1) | 1(1) |
| C(50) | 21(1) | 38(2) | 22(1) | -1(1) | 2(1) | 4(1) |
| C(39) | 23(1) | 16(1) | 27(1) | -7(1) | -2(1) | 1(1) |
| C(45) | 21(1) | 40(2) | 36(1) | -15(1) | -5(1) | -10(1) |
| C(24) | 21(1) | 29(1) | 39(2) | -12(1) | -7(1) | -6(1) |
| C(42) | 30(1) | 24(1) | 46(2) | -18(1) | -2(1) | 0(1) |
| C(44) | 23(1) | 26(1) | 43(2) | -8(1) | 0(1) | -9(1) |
| C(26) | 18(1) | 56(2) | 31(1) | -10(1) | 0(1) | -10(1) |
| C(15) | 31(2) | 27(1) | 78(2) | -32(2) | -14(1) | 3(1) |
| C(25) | 19(1) | 36(1) | 40(2) | -16(1) | -10(1) | 4(1) |
| C(13) | 26(1) | 18(1) | 47(2) | -14(1) | -11(1) | 2(1) |
| C(41) | 36(2) | 20(1) | 39(2) | -11(1) | 9(1) | 2(1) |
| C(40) | 31(1) | 25(1) | 40(2) | -9(1) | -12(1) | 8(1) |
| C(16) | 24(1) | 26(1) | 97(3) | -31(2) | -11(2) | 6(1) |
| C(14) | 73(2) | 28(2) | 59(2) | -7(1) | -30(2) | 16(2) |

Table S10. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for compound **3**_0m_a.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(37) | 3540 | 3204 | 2636 | 24 |
| H(35) | 4198 | 2128 | 5441 | 27 |
| H(34) | 5821 | 2913 | 4779 | 25 |
| H(19) | 11040 | 6561 | 2865 | 27 |
| H(38) | 5173 | 3990 | 1961 | 24 |
| H(22) | 9302 | 6778 | 337 | 23 |
| H(21) | 11077 | 7256 | -114 | 24 |
| H(12) | 4074 | 7989 | 3179 | 22 |
| H(30) | 7819 | 659 | 2617 | 24 |
| H(18) | 9276 | 6073 | 3326 | 24 |
| H(46A) | 2321 | 2544 | 5894 | 45 |
| H(46B) | 1208 | 2372 | 5693 | 45 |
| H(46C) | 1804 | 3397 | 5012 | 45 |
| H(28) | 10651 | 2024 | 1619 | 22 |
| H(31) | 6869 | 2105 | 2876 | 23 |
| H(10) | 6851 | 9431 | 1733 | 28 |
| H(9) | 7845 | 7894 | 1830 | 25 |
| H(45A) | 1201 | 2016 | 4147 | 47 |
| H(45B) | 2300 | 2021 | 3300 | 47 |
| H(45C) | 1757 | 3062 | 3463 | 47 |
| H(24A) | 13550 | 7792 | 1361 | 43 |
| H(24B) | 12497 | 7479 | 2271 | 43 |
| H(24C) | 12402 | 8414 | 1241 | 43 |
| H(42A) | 8710 | -732 | 2564 | 50 |
| H(42B) | 9688 | -1130 | 1816 | 50 |
| H(42C) | 8869 | -193 | 1353 | 50 |
| H(44A) | 3119 | 881 | 5700 | 49 |
| H(44B) | 3181 | 681 | 4671 | 49 |
| H(44C) | 2035 | 701 | 5454 | 49 |
| H(26A) | 12637 | 8043 | -400 | 55 |

| | | | | |
|---|---|---|---|---|
| H(26B) | 12867 | 6886 | -358 | 55 |
| H(26C) | 13772 | 7433 | -202 | 55 |
| H(15A) | 5194 | 10202 | 3415 | 62 |
| H(15B) | 4804 | 11223 | 2590 | 62 |
| H(15C) | 5975 | 10664 | 2313 | 62 |
| H(25A) | 13845 | 5977 | 1394 | 46 |
| H(25B) | 12880 | 5461 | 1290 | 46 |
| H(25C) | 12784 | 5706 | 2302 | 46 |
| H(41A) | 10435 | 905 | 344 | 53 |
| H(41B) | 11180 | -109 | 771 | 53 |
| H(41C) | 11350 | 920 | 905 | 53 |
| H(40A) | 11049 | 158 | 2798 | 50 |
| H(40B) | 11003 | -918 | 2698 | 50 |
| H(40C) | 10033 | -512 | 3445 | 50 |
| H(16A) | 3189 | 9445 | 2556 | 71 |
| H(16B) | 3148 | 10502 | 2726 | 71 |
| H(16C) | 3470 | 9455 | 3563 | 71 |
| H(14A) | 5544 | 10567 | 767 | 83 |
| H(14B) | 4382 | 11151 | 1019 | 83 |
| H(14C) | 4458 | 10078 | 873 | 83 |

## Computational Studies

Single point energy calculations on compounds **1-3** were conducted using the Guassian09 program [3] using the geometries and methods and basis sets as recently reported (B3LYP 6-31+g(d,p) and SDD pseudopotential for iodine).[4] Bond critical points were analyzed using Multiwfn[5] and visualized using AIMALL.[6] Visualization of the non-covalent interactions (NCI plots) were conducted using VMD 1.94.[7]

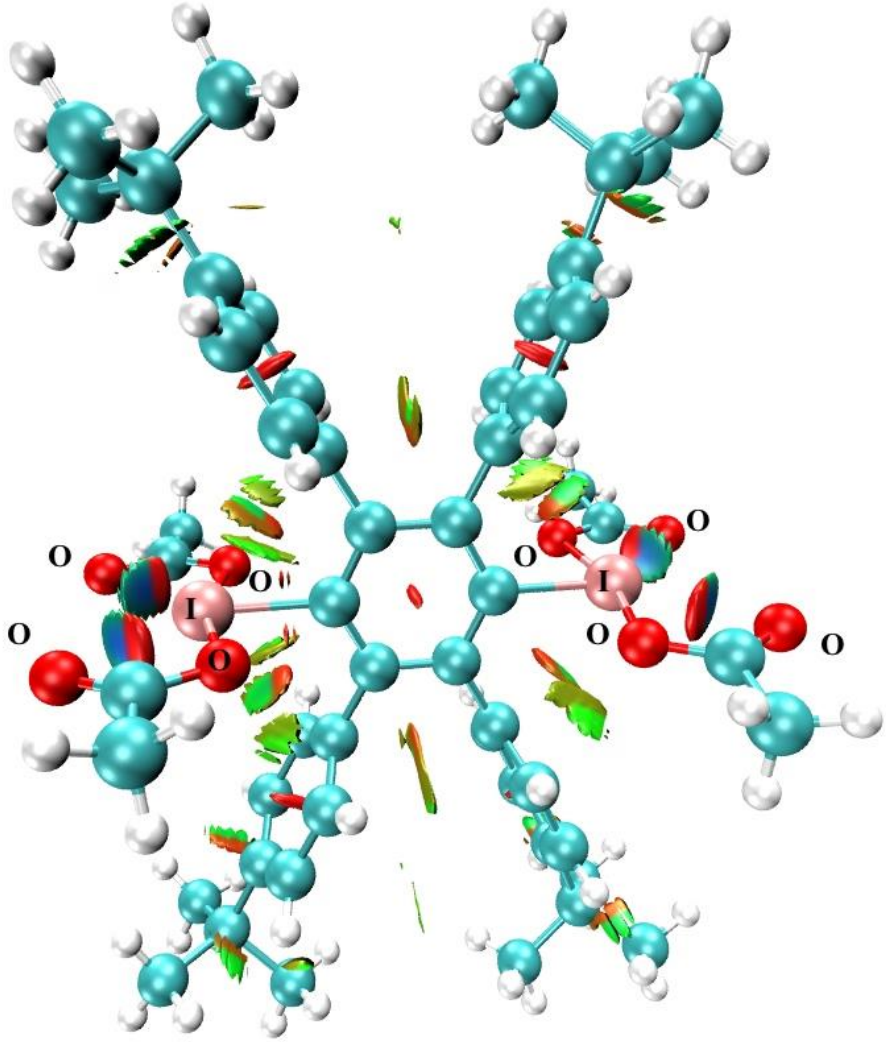



**Figure S7.**Computed NCI plots of compound **2**. The surface color red indicates repulsions, green van der Waals attractions and/or weak interactions, and blue stronger attractive interactions.

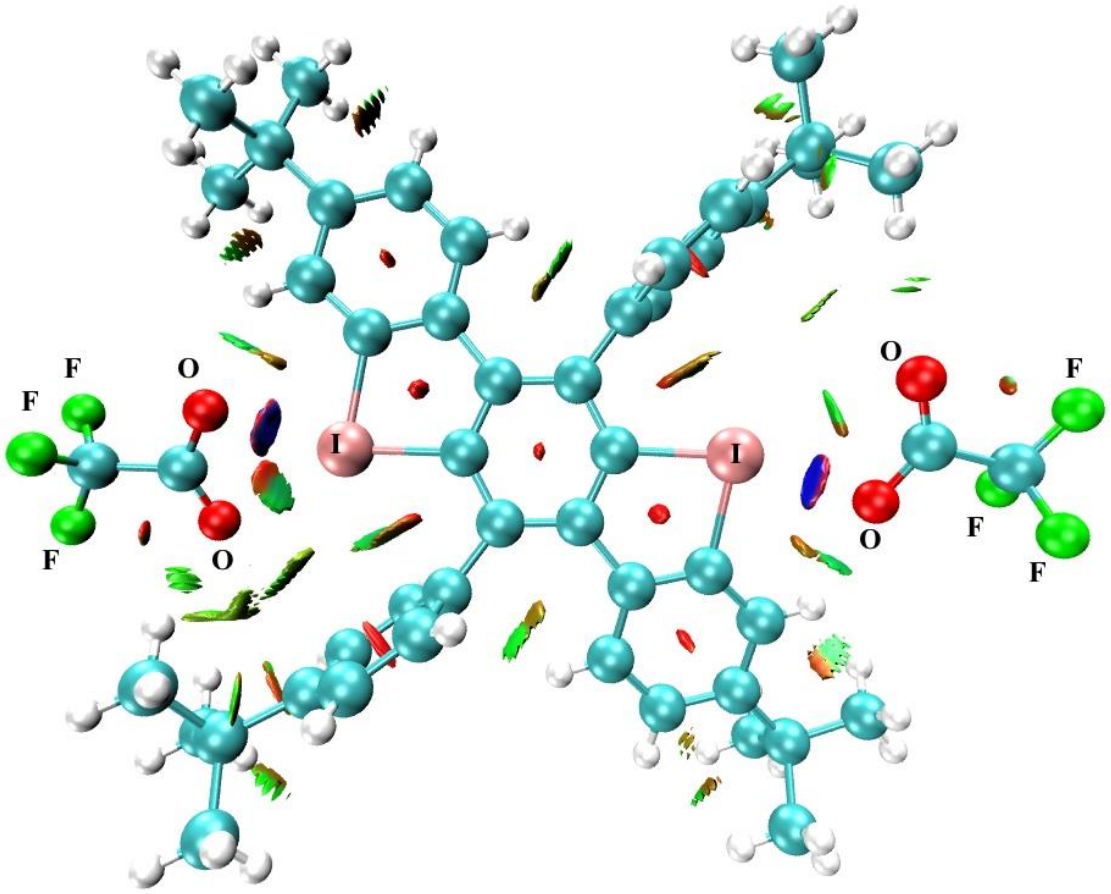



**Figure S8.**Computed NCI plots of compound **3**. The surface color red indicates repulsions, green van der Waals attractions and/or weak interactions, and blue stronger attractive interactions.

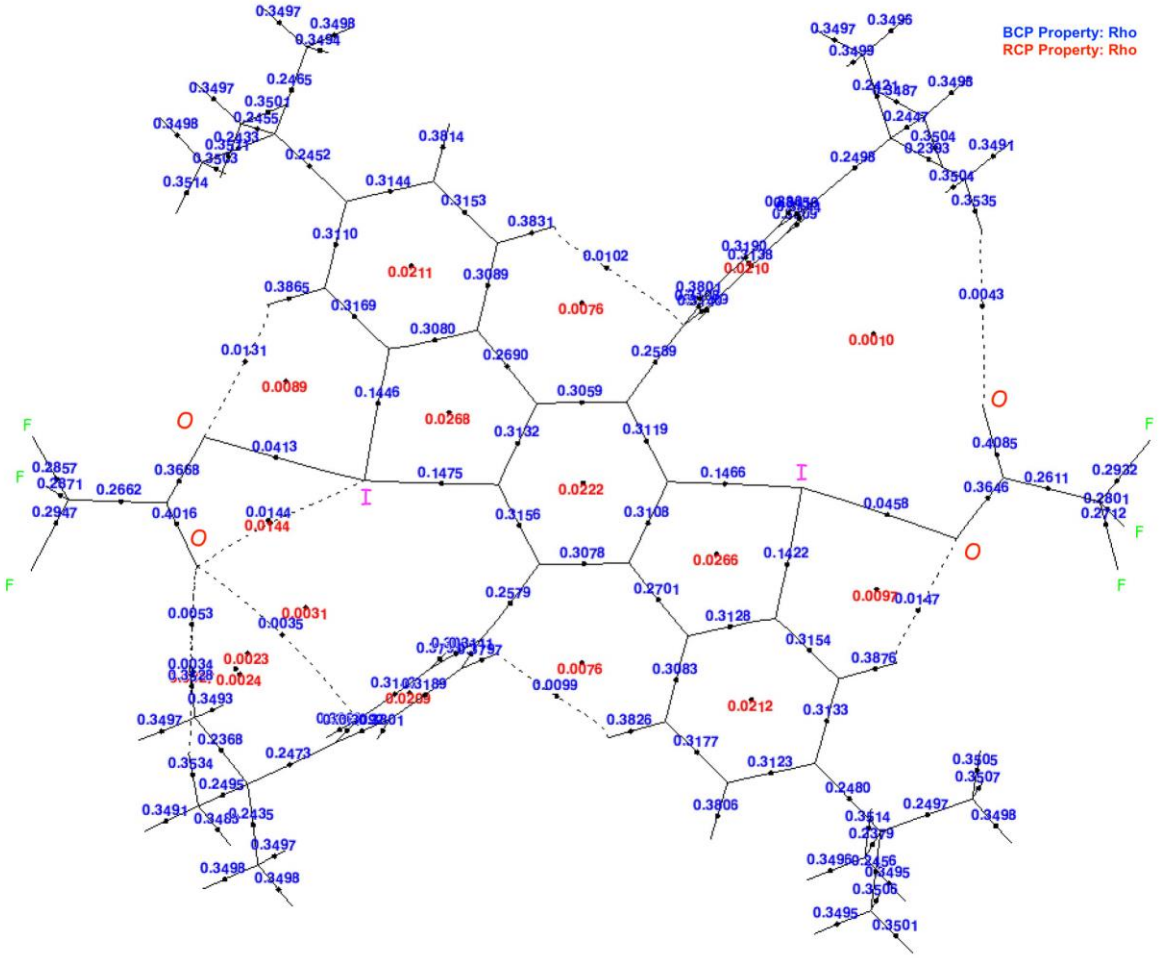



**Figure S9.**Computed NCI plots of compound **3**.

# References


1. Shah, S.; Eichler, B.E.; Smith, R.C.; Power, P.P.; Protasiewicz, J.D. *New J. Chem*. **2003**, 27, 442–445.

2. Watanabe, A.; Miyamoto, K.; Okada, T.; Asawa, T.; Uchiyama, M. *J. Org. Chem*. **2018**, 83, 14262−14268.

3. Gaussian 09, Revision C.01, Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Petersson, G.A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A.; Bloino, J.; Janesko, B.G.; Gomperts, R.; Mennucci, B.; Hratchian, H.P.; Ortiz, J.V.; Izmaylov, A.F.; Sonnenberg, J.L.; Williams-Young, D.; Ding, F.; Lipparini,F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V.G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J.A.; Peralta, J.E.; Ogliaro, F.; Bearpark, M.; Heyd, J.; Brothers, E.; Kudin, K.N.; Staroverov, V.N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J.C.; Iyengar, S.S.; Tomasi, J.; Cossi, M.; Millam, J.M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J.W.; Martin, R.L.; Morokuma, K.; Farkas, O.; Foresman, J.B.; Fox, D.J. Gaussian, Inc., Wallingford CT, **2016**.

4. Radzhabov, M.R.; Sheremetev, A.B.; Pivina, T.S. Oxidative ability of organic iodine(iii) reagents: a theoretical assessment. *New J. Chem.,* **2020**, 44, 7051-7057.

5. Lu, T.; Chen, F. Multiwfn: A Multifunctional Wavefunction Analyzer, *J. Comput. Chem*., **2012**, 33, 580-592.

6. AIMAll (Version 19.10.12), Todd A. Keith, TK Gristmill Software, Overland Park KS, USA, **2019** (aim.tkgristmill.com)

7. Humphrey, W.; Dalke, A.; Schulten, K. "VMD - Visual Molecular Dynamics", *J. Molec. Graphics*, **1996**, 14, 33-38.