# Supporting Information

for

# Copper ion salts of arylthiotetrathiafulvalenes: synthesis, structure diversity and magnetic properties

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## Selected crystallographic data, crystal structures of $2 \cdot CuBr_4$ and $7 \cdot CuBr_2$, and variations of molecular geometries of TTFs at different oxidation states

## Materials and general methods

$CuBr_2$ was purchased from Shanghai Xinbao Fine Chemical Factory (Shanghai, China). tetrahydrofuran(THF) and acetonitrile ($CH_3CN$) were distilled over $CaH_2$ and stored under $N_2$ atomsphere. **1**–**7** were synthesized by following our previous report [1].

The electrochemical properties of **1**–**7** were recorded on a RST 5000 electrochemical workstation at a scan rate of 50 mV $s^{-1}$, with glassy carbon discs as the working electrode, Pt wire as the counter electrode, and SCE electrode as the reference electrode. The concentration was $5 \times 10^{-4}$ mol $L^{-1}$ in $CH_2Cl_2$, and the supporting electrolyte was $(n\text{-Bu})_4N \cdot PF_6$ (0.1 mol $L^{-1}$). The measurement was performed at 20 $^oC$ after bubbling the solution with $N_2$ gas for 15 min.

The X-ray diffraction measurement was carried out on SuperNova (Agilent) type diffractometer. The crystal structure was solved by solved by a direct method SIR2004 [2] and refined by full-matrix least-squares method on $F^2$ by means of SHELXL-97 [3]. The X-Ray powder diffraction (XRPD) pattern was recorded on X'Pert PRO (PANalytical). The temperature dependence of the magnetic susceptibility was measured on a SQUID magnetometer of Quantum Design MPMS-XL applying a magnetic field of 1000 Oe. The data were corrected for core diamagnetism estimated from the sum of the Pascal constants [4].

## References


[1] a) Sun, J.; Lu, X.; Shao, J.; Li, X.; Zhang, S.; Wang, B.; Zhao, J.; Shao, Y.; Fang, R.; Wang, Z.; Yu, W.; Shao, X. *Chem. Eur. J.* **2013**, *19*, 12517; doi: 10.1002/chem.201301819 b) Sun, J.; Lu, X.; Shao, J.; Cui, Z.; Shao, Y.; Jiang, G.; Yu, W.; Shao, X. *RSC Adv.* **2013**, *3*, 10193. doi: 10.1039/C3RA41349G

[2] Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; de Caro, L.; Giacovazzo, C.; Polidori, G.; Spagna, R. *J. Appl. Cryst.* **2005,** *38*, 381–388. doi: 10.1107/S0021889 80403225X

[3] Sheldrick, G. M. *SHELXL-97, A Program for Crystal Structure Refinement.* University of Göttingen, Göttingen, Germany, **1997**.

[4] Gupta, R. R.; *Landolt-Bornstein, New Sreies II* (Eds: K, -H. Hellwege, A. M. Hellwege), Springer Verlag, Berlin, **1986**, vol. 16 (Diamagnetism Susceptibility)

**Table S1:** Selected crystallographic data for **1**·$CuBr_4$, **2**·$CuBr_4$, and **3**·$(CuBr_4)_{0.5}$·$CuBr_3$·THF.

| | **1**·$CuBr_4$ | **2**·$CuBr_4$ | **3**·$(CuBr_4)_{0.5}$·$CuBr_3$·THF | |
|---|---|---|---|---|
| CCDC number | 1046215 | 1046216 | 1046217 | 1046218 |
| Empirical formula | $C_{30}H_{20}S_8CuBr_4$ | $C_{34}H_{28}S_8CuBr_4$ | $C_{76}H_{72}O_2S_{16}Cu_3Br_{10}$ | $C_{76}H_{72}O_2S_{16}Cu_3Br_{10}$ |
| Formula weight | 1020.12 | 1076.22 | 2520.02 | 2520.02 |
| Temperature / K | 293(2) | 293(2) | 173(2) | 291(2) |
| $\lambda$ / Å | 1.54184 | 0.71073 | 0.71073 | 0.71073 |
| Crystal size / $mm^3$ | 0.31×0.05×0.04 | 0.21×0.02×0.02 | 0.22×0.07×0.07 | 0.22×0.07×0.07 |
| Crystal system | Orthorhombic | Monoclinic | Triclinic | Triclinic |
| space group | *P* bcn | *I*2/a | *P*-1 | *P*-1 |
| *a* / Å | 21.0945(5) | 13.9096(7) | 13.0164(6) | 13.1368(5) |
| *b* / Å | 13.8077(7) | 14.1046(7) | 13.3435(6) | 13.4389(5) |
| *c* / Å | 12.4172(2) | 21.0770(10) | 14.5787(7) | 14.8346(5) |
| $\alpha$ / ° | 90.00 | 90.00 | 102.051(6) | 101.664(3) |
| $\beta$ / ° | 90.00 | 107.985(6) | 92.764(6) | 93.457(3) |
| $\gamma$ / ° | 90.00 | 90.00 | 116.503(7) | 116.863(4) |
| *V* / $Å^3$ | 3616.7(2) | 3933.0(3) | 2194.51(18) | 2253.37(14) |
| Z | 4 | 4 | 1 | 1 |
| $d_{calc}$ / $g·cm^{-3}$ | 1.873 | 1.818 | 1.907 | 1.857 |
| $\mu$ / $mm^{-1}$ | 10.522 | 5.069 | 5.698 | 5.549 |
| $2\theta_{max}$ / ° | 145.34 | 57.34 | 57.74 | 57.82 |
| Data / restraints / parameters | 3582/0/195 | 4302/0/213 | 10203/0/488 | 10331/0/488 |
| *GooF* | 1.045 | 0.974 | 1.035 | 1.011 |
| *R* [I>2σ(I)] | 0.0458 | 0.0494 | 0.0532 | 0.0591 |
| $wR_2$ | 0.1168 | 0.0831 | 0.1133 | 0.1228 |

**Table S2:** Selected crystallographic data for **4**·$CuBr_4$, **5**·$Cu_2Br_6$, **6**·$CuBr_2$·$CH_3CN$, and **7**·$CuBr_2$.

| | **4**·$CuBr_4$ | **5**·$Cu_2Br_6$ | **6**·$CuBr_2$·$CH_3CN$ | **7**·$CuBr_2$ |
|---|---|---|---|---|
| CCDC number | 1046219 | 1046220 | 1046221 | 1046222 |
| Empirical formula | $C_{34}H_{28}O_4S_8CuBr_4$ | $C_{34}H_{28}O_4S_8Cu_2Br_6$ | $C_{40}H_{28}NO_8S_8CuBr_2$ | $C_{42}H_{36}O_8S_8CuBr_2$ |
| Formula weight | 1140.22 | 1363.58 | 1130.48 | 1148.55 |
| Temperature / K | 293(2) | 293(2) | 293(2) | 293(2) |
| $\lambda$ / Å | 0.71073 | 1.54184 | 0.71073 | 0.71073 |
| Crystal size / $mm^3$ | 0.31×0.05×0.05 | 0.31×0.22×0.11 | 0.35×0.21×0.15 | 0.35×0.22×0.15 |
| Crystal system | Orthorhombic | Triclinic | Triclinic | Triclinic |
| space group | *P*ccn | *P*-1 | *P*-1 | *P*-1 |
| *a* / Å | 12.9103(8) | 8.8766(5) | 8.0605(3) | 12.8898(12) |
| *b* / Å | 19.5008(5) | 11.3774(5) | 11.1170(7) | 14.8147(13) |
| *c* / Å | 16.3696(5) | 12.1805(5) | 13.7852(6) | 14.8279(13) |
| $\alpha$ / ° | 90.00 | 92.375(3) | 89.253(4) | 107.327(8) |
| $\beta$ / ° | 90.00 | 105.574(4) | 88.684(4) | 93.858(7) |
| $\gamma$ / ° | 90.00 | 112.882(4) | 80.707(4) | 115.350(9) |
| *V* / $Å^3$ | 4121.2(3) | 1076.89(9) | 1218.68(10) | 2379.7(3) |
| Z | 4 | 1 | 1 | 2 |
| $d_{calc}$ / $g·cm^{-3}$ | 1.838 | 2.103 | 1.540 | 1.603 |
| $\mu$ / $mm^{-1}$ | 4.850 | 11.681 | 2.478 | 2.538 |
| $2\theta_{max}$ / ° | 57.1 | 145.28 | 57.26 | 57.18 |
| Data / restraints / parameters | 4816/0/231 | 4230/0/245 | 5499/0/286 | 10692/0/550 |
| *GooF* | 1.004 | 1.062 | 1.037 | 1.085 |
| *R* [I>2σ(I)] | 0.0516 | 0.0354 | 0.0601 | 0.0839 |
| $wR_2$ | 0.0704 | 0.0899 | 0.1618 | 0.2016 |

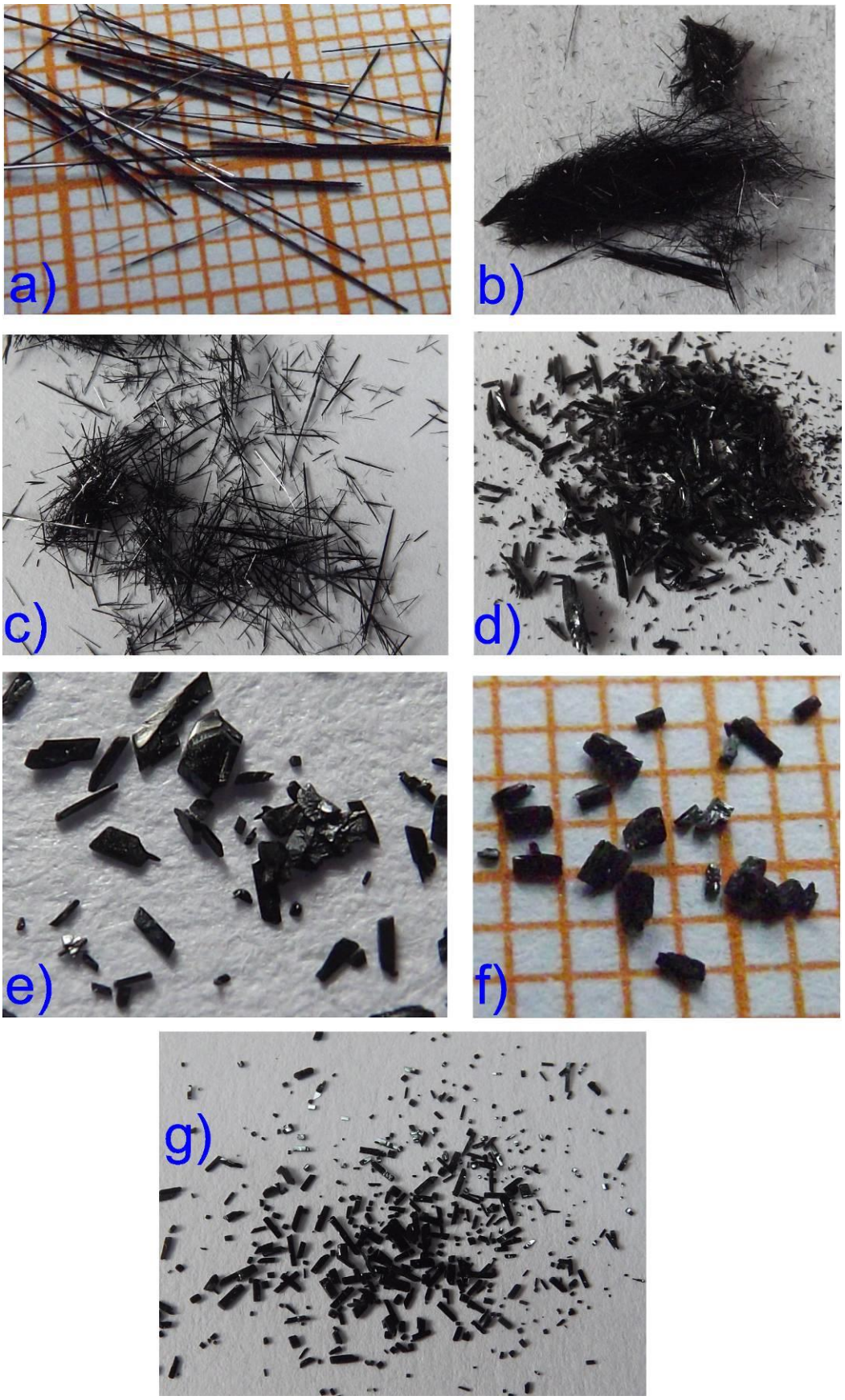


**Figure S1:** Photographs for the single crystals of salts: a) **1**·$CuBr_4$; b) **2**·$CuBr_4$; c) **3**·$(CuBr_4)_{0.5}$·$CuBr_3$·THF; d) **4**·$CuBr_4$; e) **5**·$Cu_2Br_6$; f) **6**·$CuBr_2$·$CH_3CN$; g) **7**·$CuBr_2$.

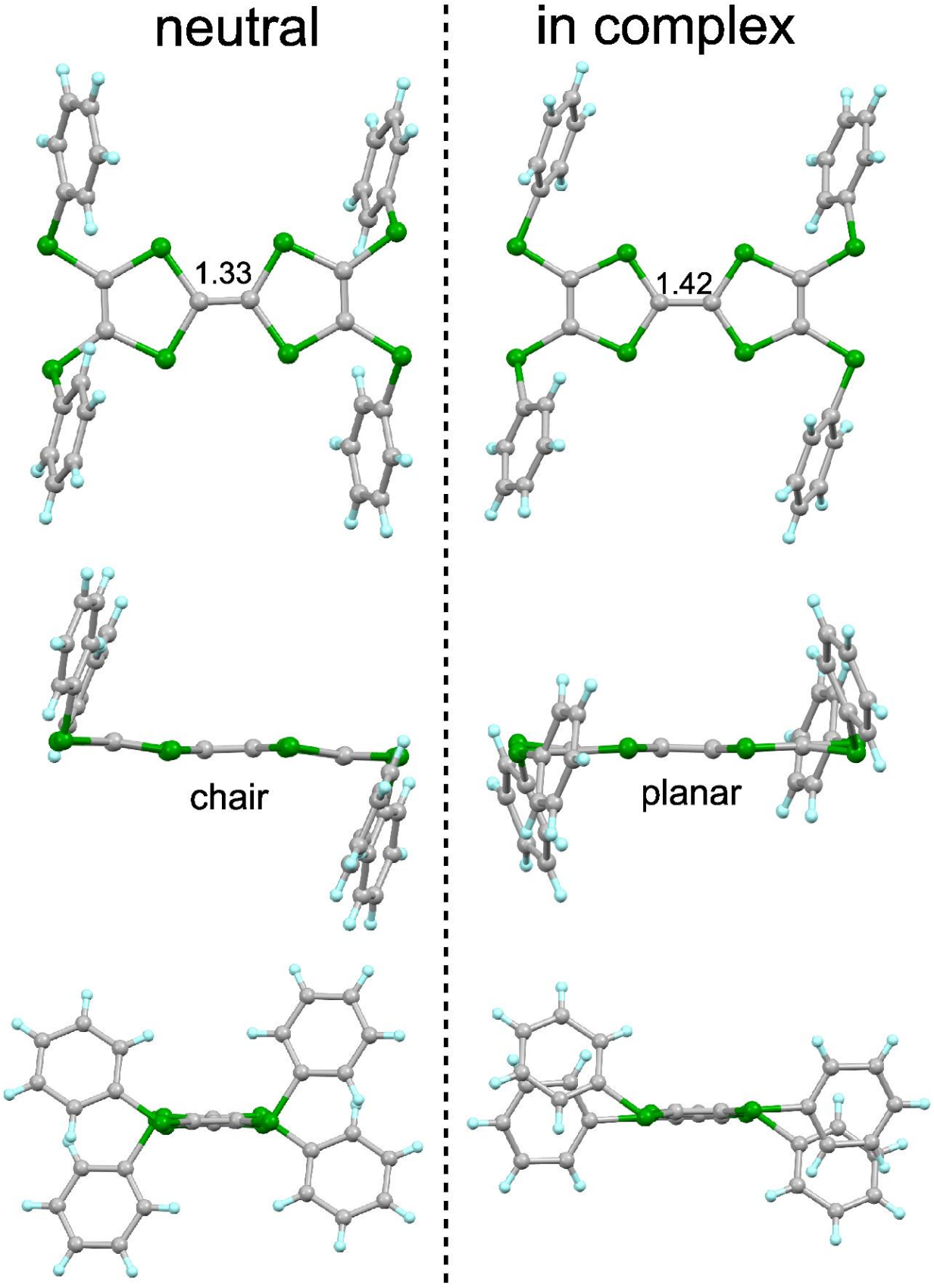


**Figure S2:** Comparison of the molecular geometry of **1** in the neutral state and in **1**·$CuBr_4$.

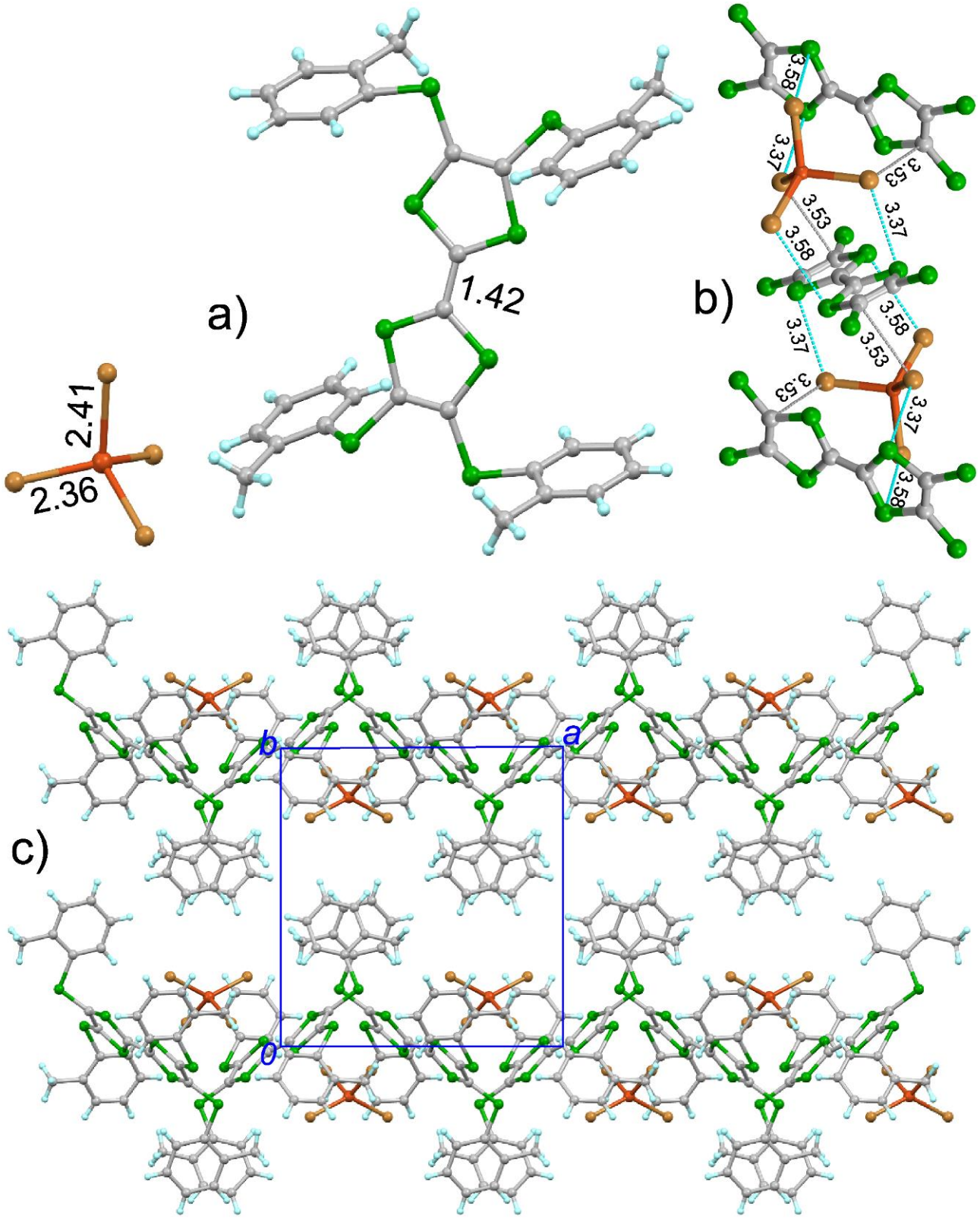


**Figure S3:** Crystal structure of **2**·$CuBr_4$: a) unit cell contents with the typical bond lengths shown (in unit of Å); b) interaction between $[Cu(II)Br_4]^{2-}$ ion and the central TTF core of **2**, where the cyan and grey dashed lines represent Br···S and Br···C contacts (Å), respectively; c) the packing structure viewed along the *a*-axis.

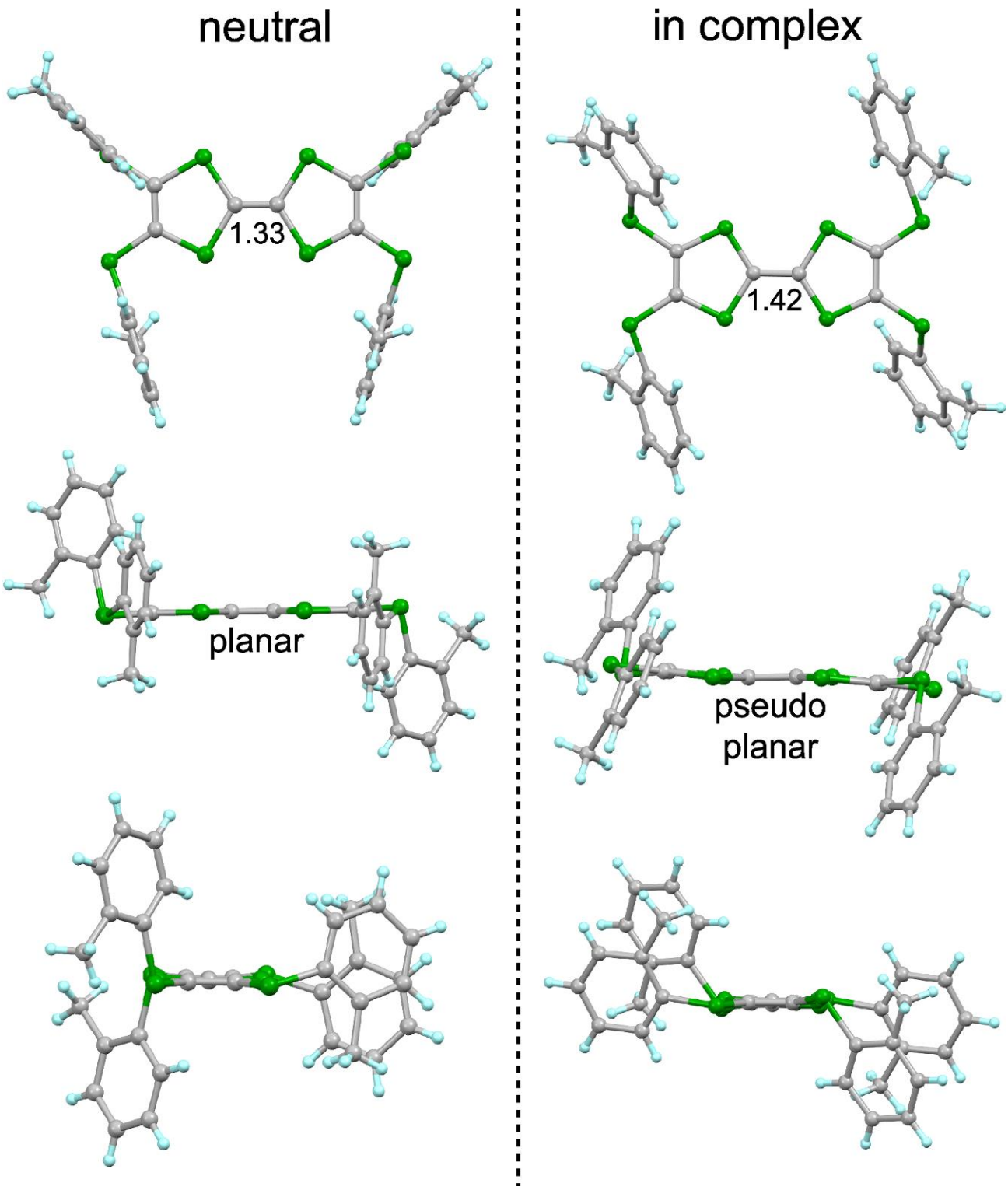


**Figure S4:** Comparison of the molecular geometry of **2** in the neutral state and in **2**·$CuBr_4$.

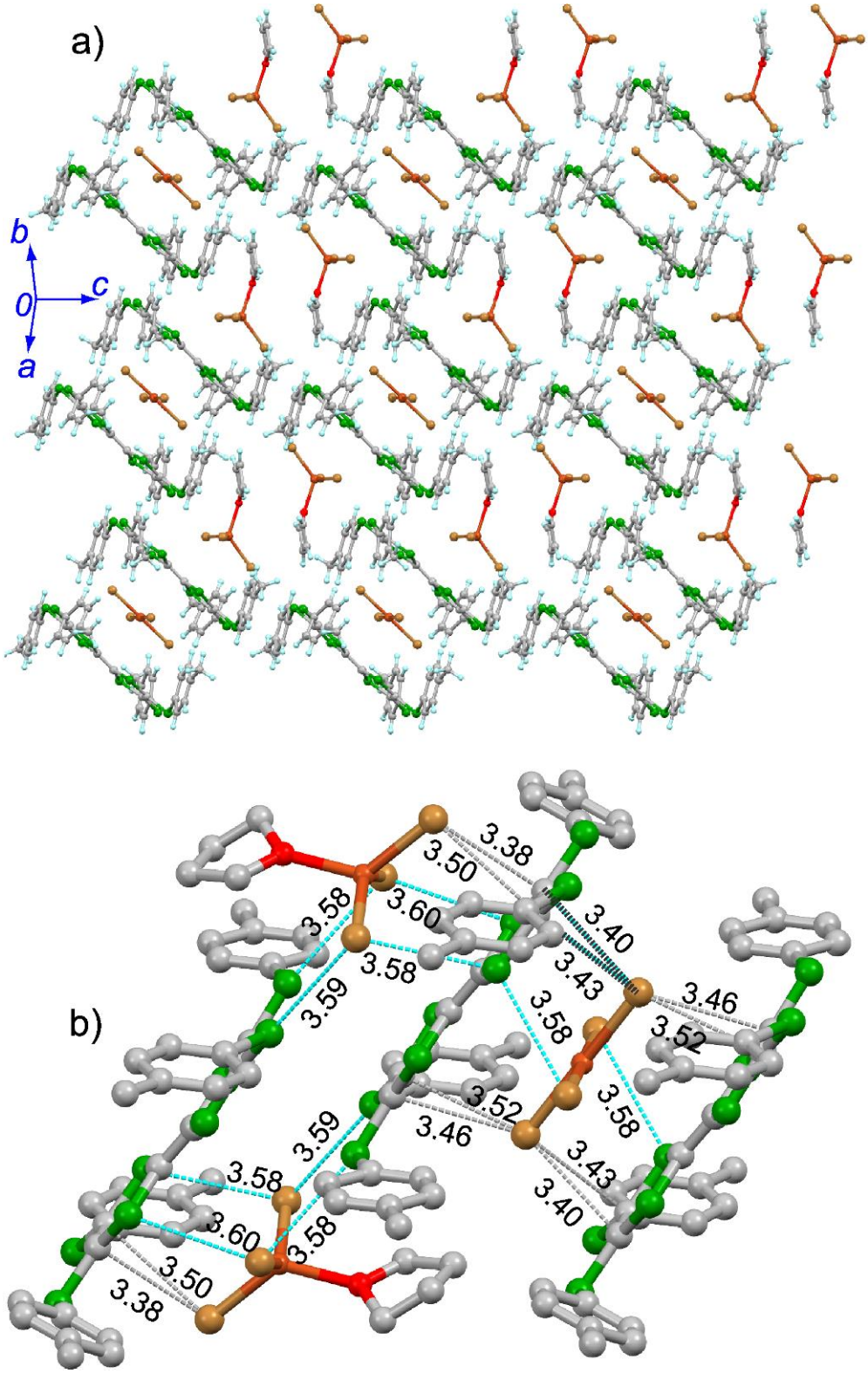


**Figure S5:** Crystal structure of **3**·$(CuBr_4)_{0.5}$·$CuBr_3$·THF at 173 K: a) packing structure; b) interaction between the anions and the central TTF core of **3**, where cyan and grey dashed lines represent Br···S and Br···C contacts (Å), respectively. In comparison with the structure at 291 K, the intermolecular interactions between **3** and anions at 173 K are significantly strengthened.

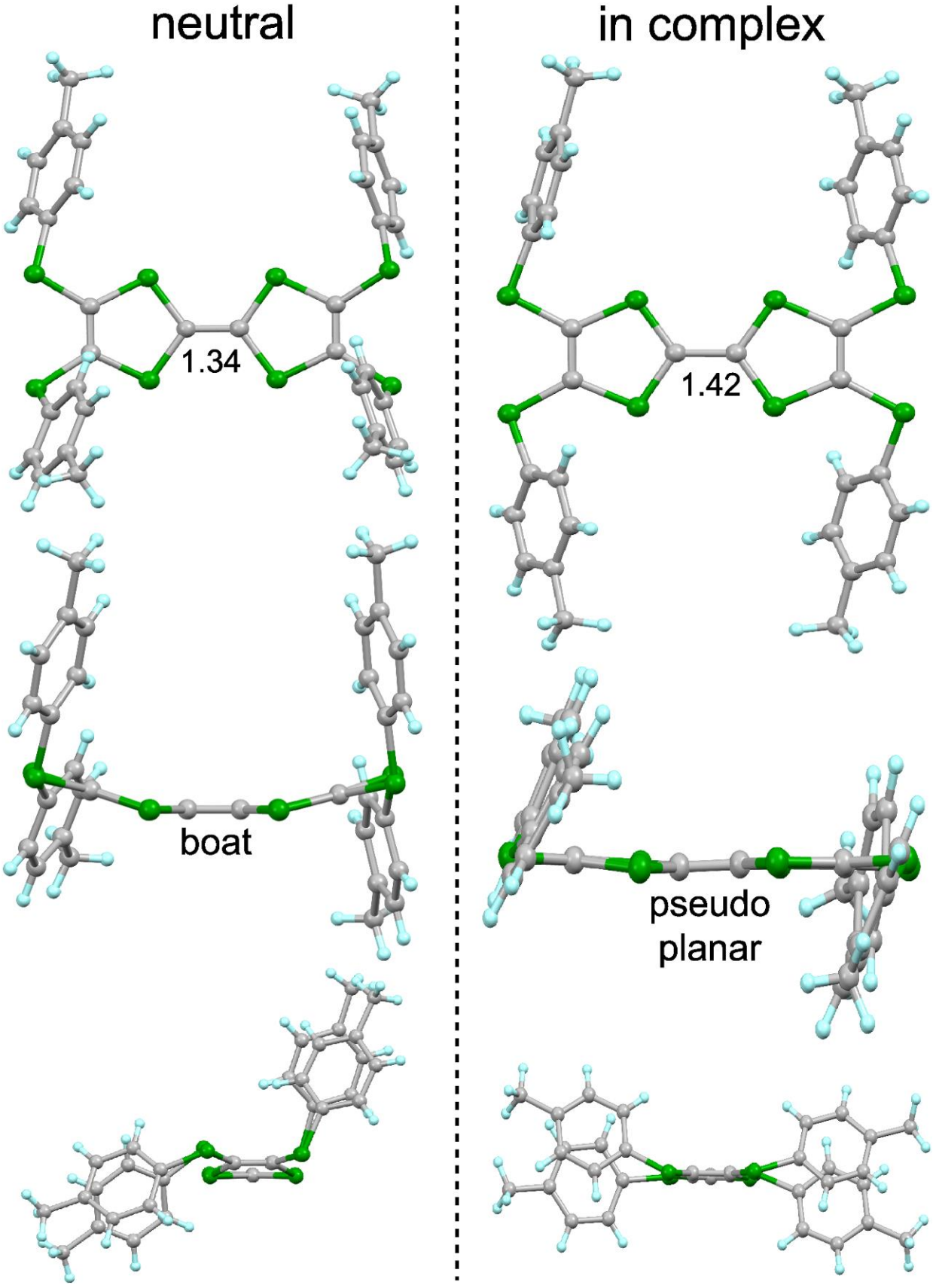


**Figure S6:** Comparison of the molecular geometry of **3** in neutral state and in **3**·$(CuBr_4)_{0.5}$·$CuBr_3$·THF.

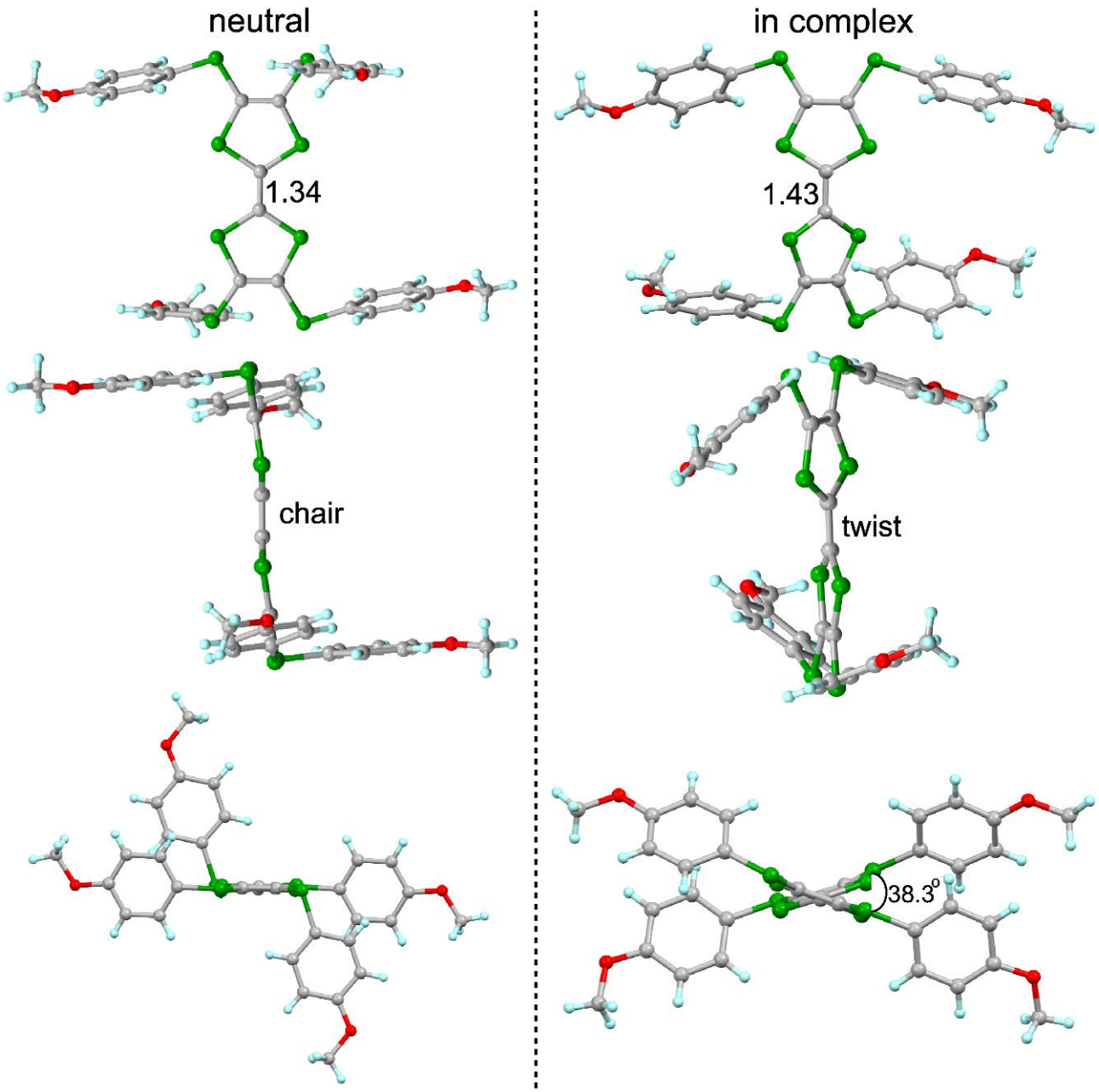


**Figure S7:** Comparison of the molecular geometry of **4** in the neutral state and in **4**·$CuBr_4$.

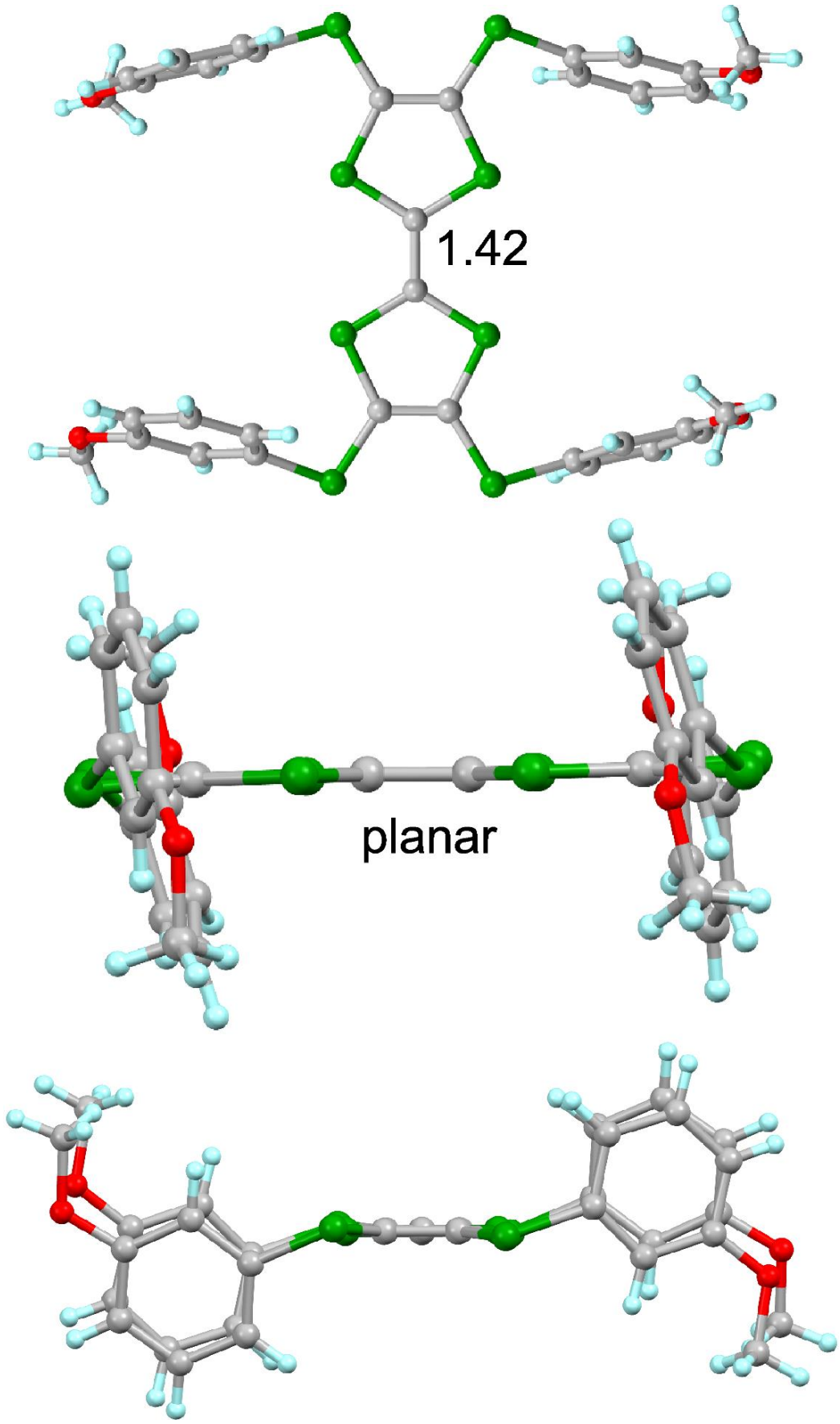


**Figure S8:** Molecular geometry of **5** in **5**·$Cu_2Br_6$.

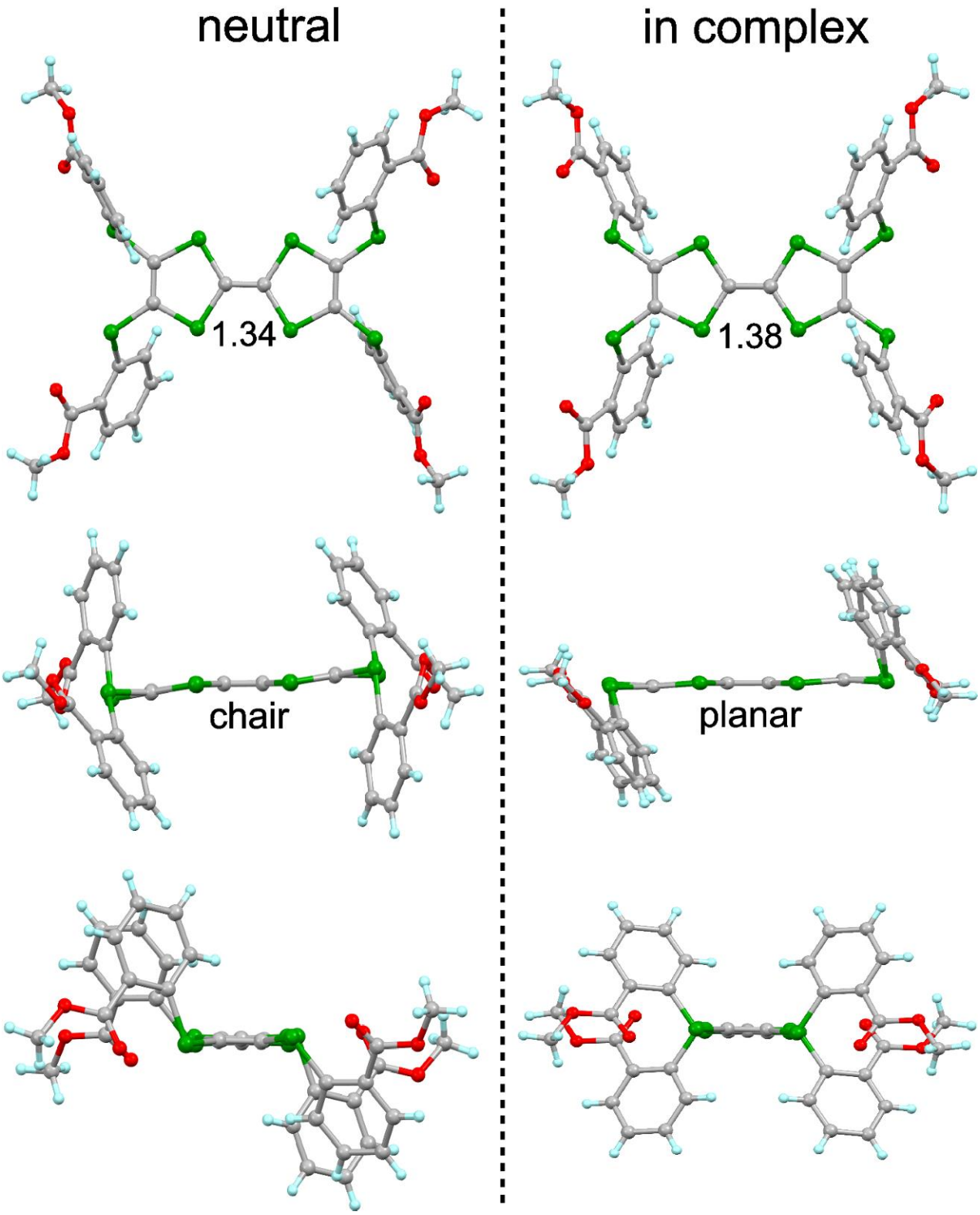


**Figure S9:** Comparison of the molecular geometry of **6** in neutral state and in **6**·$CuBr_2$·$CH_3CN$.

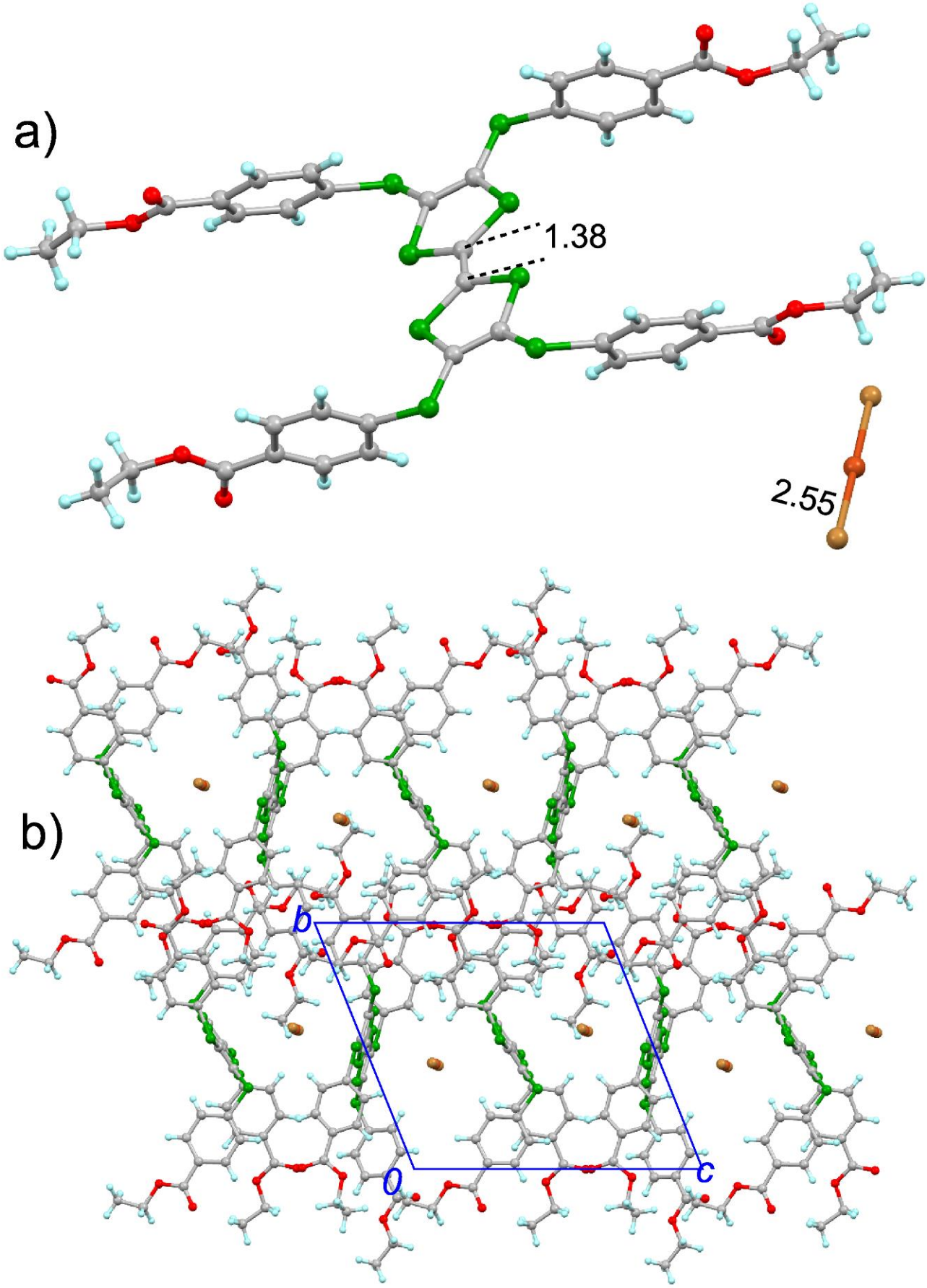


**Figure S10:** Crystal structure of **7**·$CuBr_2$: a) unit cell contents with the typical bond lengths shown (Å); b) packing structure viewed along the crystallographic *a*-axis.

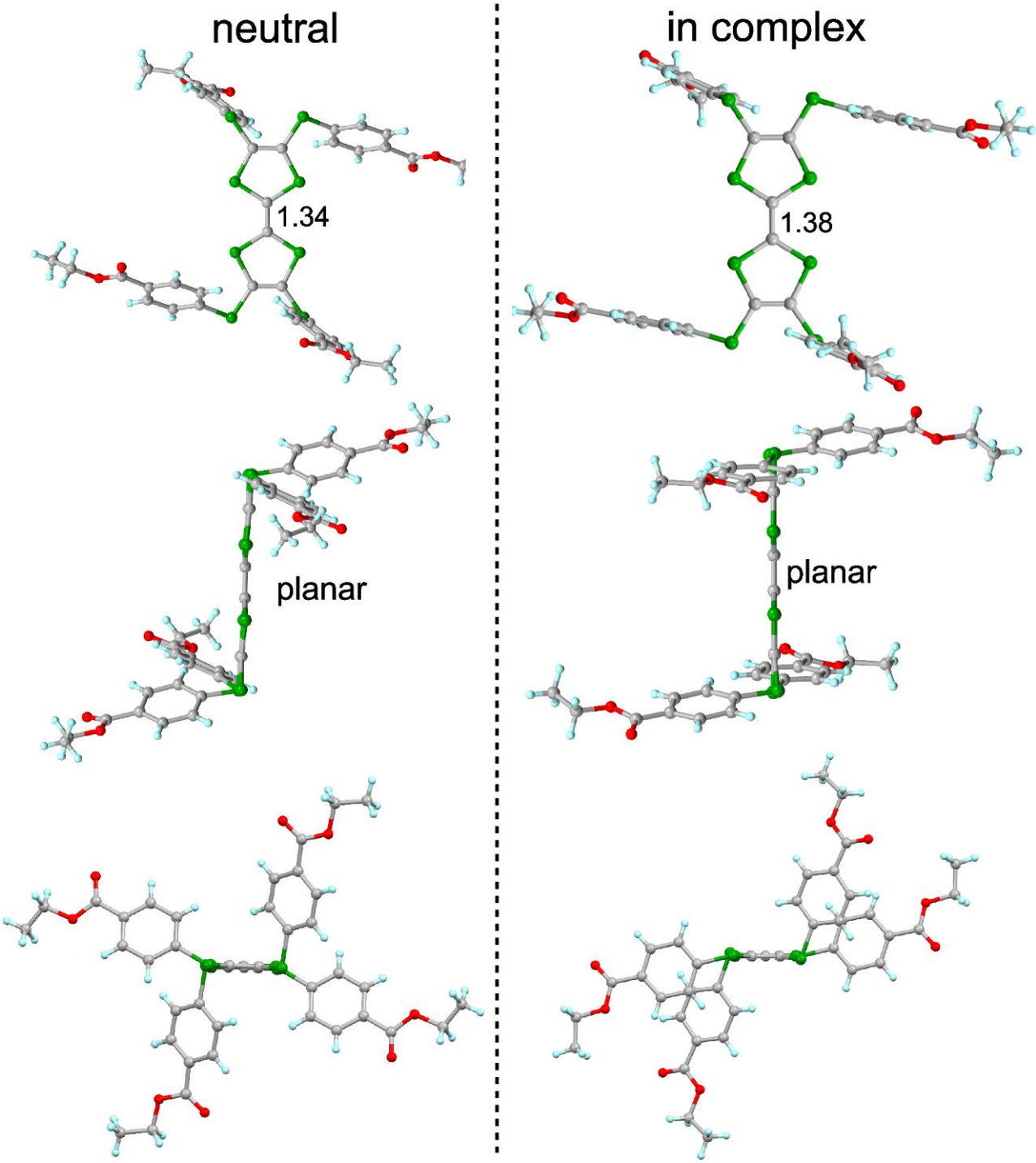


**Figure S11:** Comparison of the molecular geometry of **7** in the neutral state and in **7**·$CuBr_2$.