Supplementary Material For

Charge-transfer complexs of arylthiotetrathiafulvalenes and $TCNQF_4$ with structure diversity and electron states

Longfei Ma[A, C] and Congjie Pan[B]

[A] Department of Criminal Science and Technology, Henan Police College Zhengzhou, 450046, P. R. China

[B] School of Pharmacy, Henan University of Chinese Medicine, Zhengzhou, 450046, P. R. China

[C] Corresponding author. Email: malongfei@hnp.edu.cn.

UV-Vis absorption spectra, crystallographic data, crystal structures of $3 \cdot TCNQF_4$ and $4 \cdot TCNQF_4$, and variations of molecular geometries of Ar-S-TTFs in different complexes

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Materials and general methods

The Ar-s-TTF (1-5) were synthesized according to previous report [1-2], and they were recrystallized from appropriate solvents to gain high purity. The solvents were purified by following the standard procedure. $TCNQF_4$ was purchased from energy chemical (Shanghai, China).

Using glassy carbon disk as working electrode, platinum wire as counter electrode and SCE electrode as reference electrode, the electrochemical properties of 1-5 were recorded at the scanning rate of 50 mV s^{-1} on RST 5000 electrochemical workstation. The supporting electrolyte was $(n\text{-}Bu)_4N{\cdot}PF_6$ (0.1 mol L^{-1}) and the concentration was 5×10^{-4} mol L^{-1} in CH_2Cl_2. The measurement was carried out after bubbling with N_2 gas for 10 minutes at 20 °C. UV-Vis spectra of 1-5 in CH_2Cl_2 solution (2×10^{-5} mol L^{-1}) were measured on UV-2006 UV-Specterophotometer at 20 °C. The solid state UV-Vis spectra were measured by dispersing the samples on the KBr pellet. Infrared (IR) spectra were obtained in transmission mode with PerkinFlmer 400 Fourier transform (FTIR) spectrometer.

The X-ray diffraction measurement was carried out on Super-Nova (Agilent) type diffractometer. The crystal structure was solved by a direct method Olex2 [3] and refined by a full matrix least-squares method on F2 by means of SHELXL-97 [4]. The calculated positions of the hydrogen atoms were included in the final refinement.

References

[1] 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.

[2] 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.

[3] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard J. A. K.; Puschmann. H. "OLEX2: a complete structure solution, refinement and analysis program". *J. Appl. Cryst.*, **2009**, *42*, 339. doi:10.1107/S0021889808042726.

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

Synthesis of the complexes

Diffusion method： compound 1 (2×10^{-5} mol, 15.1 mg) dissolved in 4 mL CH_2Cl_2 in the test tube, $TCNQF_4$ (2.2×10^{-5} mol, 6.0 mg) dissolved in 4 mL CH_3CN. After that, 4 mL CH_3CN was added to the solution of 1 slowly. Then the solution of $TCNQF_4$ was added to the test tube and left standing without disruption in a dark hood at room temperature. After one week, the black columnar crystals were cropped.

evaporation method: Compound 3 (1×10^{-5} mol, 7.5 mg) and $TCNQF_4$ (1.1×10^{-5} mol, 3.0 mg) were added in 2 ml 1, 2-dichloroethane respectively and heated to 70°C for complete dissolution. Then, the solution of $TCNQF_4$ was added in solution of 3 and refluxed for 2 hours. The mixture was placed in a dark hood without disruption at room temperature for two weeks to obtain black columnar single crystals.

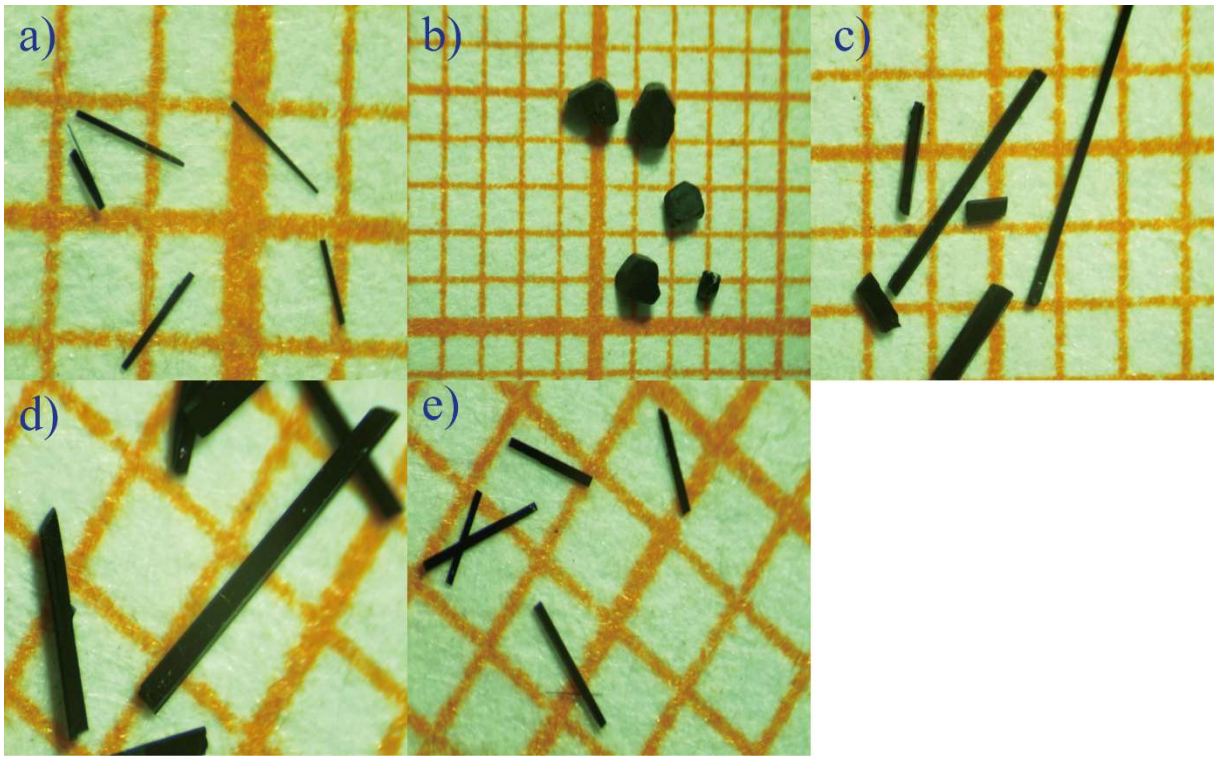


Figure S1: photographs for the single crystals of the complexes: a) 1·$TCNQF_4$, b) 2·$TCNQF_4$·$C_2H_4Cl_2$, c) 3·$TCNQF_4$, d) 4·$TCNQF_4$, e) $(5)_2$·$TCNQF_4$.

UV-Vis absorption spectra

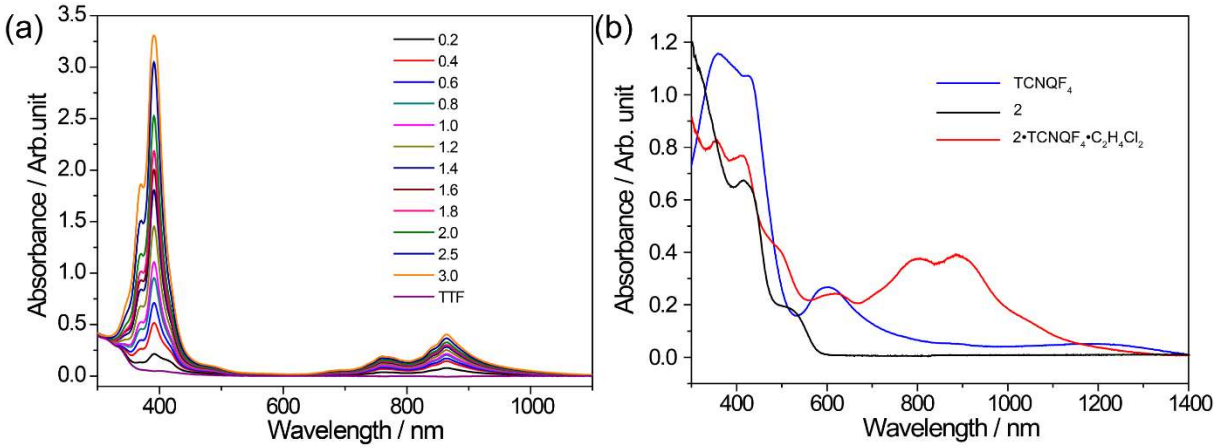


Figure S2: UV-Vis absorption spectra of a) ~~1~~ 2 upon titration with $TCNQF_4$; b) solid CT complex $2{\cdot}TCNQF_4{\cdot}C_2H_4Cl_2$.

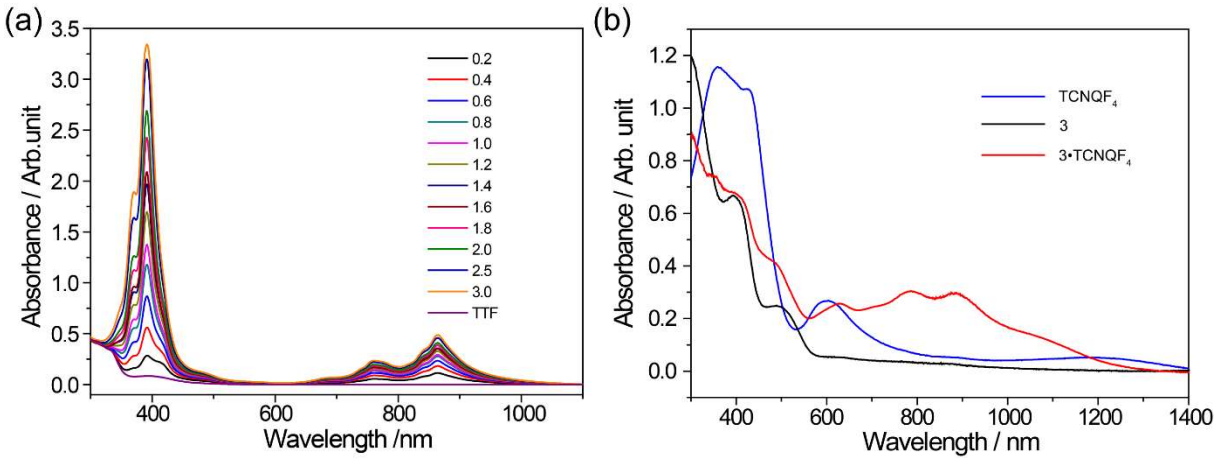


Figure S3: UV-Vis absorption spectra of a) ~~1~~ 3 upon titration with $TCNQF_4$; b) solid CT complex $3{\cdot}TCNQF_4$.

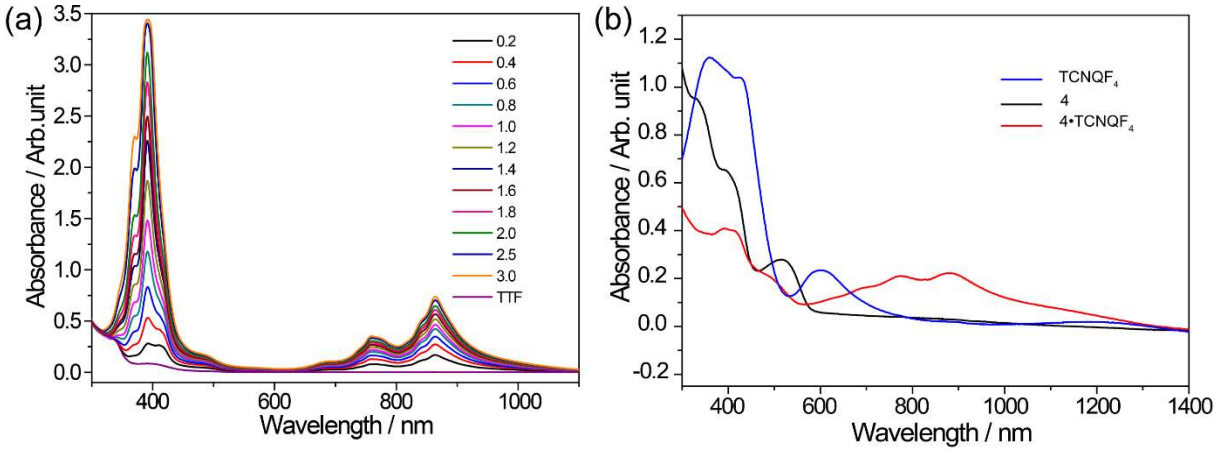


Figure S4: UV-Vis absorption spectra of a) ~~1~~ 4 upon titration with $TCNQF_4$; b) solid CT complex $4 \cdot TCNQF_4$.

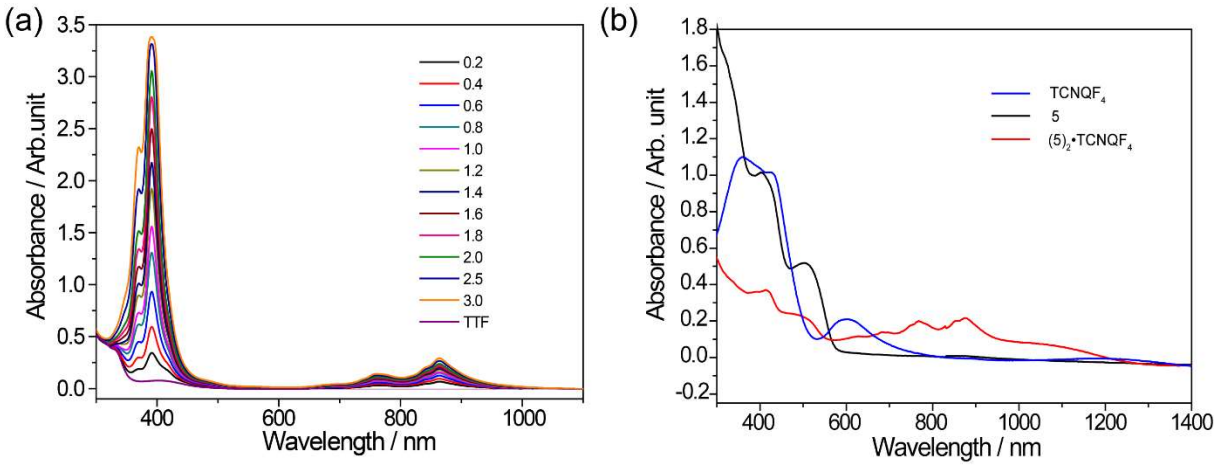


Figure S5: UV-Vis absorption spectra of a) ~~1~~ 5 upon titration with $TCNQF_4$; b) solid CT complex $(5)_2 \cdot TCNQF_4$.

Crystallographic data

Table S1: Crystallographic date for the CT complexes.

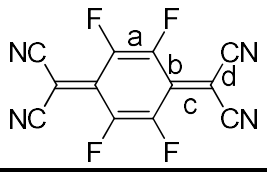
Complexes	1·$TCNQF_4$	2·$TCNQF_4$·($C_2H_4Cl_2$)	3·$TCNQF_4$
CCDC number	2103000	2102998	2103002
Empirical formula	$C_{42}H_{20}F_4N_4S_8$	$C_{48}H_{32}Cl_2F_4N_4S_8$	$C_{50}H_{36}F_4N_4S_8$
Formula weight	913.10	1068.15	1025.31
Temperature [K]	110	173	173
λ [Å]	0.71073	0.71073	0.7173
Crystal size [mm^3]	0.05×0.1×0.2	0.1×0.2×0.3	0.1×0.2×0.4
Crystal system	Monoclinic	Triclinic	Triclinic
space group	$P2_1/n$	P-1	P-1
a [Å]	5.5070(11)	9.6805(7)	8.6620(3)
b [Å]	15.088(3)	10.0453(7)	11.9902(4)
c [Å]	23.988(5)	13.5758(9	24.3664(10)
α [°]	90	95.317(6)	88.751(3)
β [°]	92.54(3)	108.661(6)	81.002(3)
γ [°]	90	109.037(7)	76.965(3)
V [$Å^3$]	1991.2(7)	1153.61(15)	2434.89(16)
Z	2	1	2
dcalc [g•cm-3]	1.523	1.538	1.398
μ [mm^{-1}]	0.506	0.561	0.422
2θmax [°]	49.982	50.054	57.28
Limiting indices	3358/0/262	4067/0/300	10989/0/603
GooF	1.150	1.085	1.073
$R[I>2\sigma(I)]$	0.0296	0.0405	0.0444
wR_2	0.0852	0.1137	0.0945

Table S2: Crystallographic date for the CT complexes.

Complexes	4·$TCNQF_4$	$(5)_2$·$TCNQF_4$
CCDC number	2103001	2102999
Empirical formula	$C_{46}H_{28}F_4N_4O_4S_8$	$C_{44}H_{36}F_2N_2O_8S_8$
Formula weight	1033.20	1015.23
Temperature [K]	173	173
λ [Å]	0.71073	0.71073
Crystal size [mm^3]	0.1×0.1×0.3	0.05×0.1×0.3
Crystal system	Triclinic	Triclinic
space group	*P*-1	*P*-1
a [Å]	10.9778(7)	9.5975(5)
b [Å]	13.8315(9)	14.0947(8)
c [Å]	15.3712(6)	17.2237(9)
α [°]	77.684(5)	73.727(5)
β [°]	87.823(4)	84.731(4)
γ [°]	72.846(6)	84.669(4)
V [$Å^3$]	2178.0(2)	2221.6(2)
Z	2	2
dcalc [g•cm^{-3}]	1.575	1.518
μ [mm-1]	0.479	0.467
2θmax [°]	57.446	57.304
Limiting indices	9849/0/599	9991/0/585
GooF	1.054	1.061
$R[I>2\sigma(I)]$	0.0437	0.0466
wR_2	0.0943	0.0959

Selected bond lengths and Nitrile Frequencies in the $TCNQF_4$

Table S3: Intramolecular distances in $TCNQF_4$ molecules and calculated charge in the complexes.



complex	a/Å	b/Å	c/Å	d/Å	δ	charge
1·$TCNQF_4$	1.362	1.424	1.421	1.431	-0.93	-1
2·$TCNQF_4$·$C_2H_4Cl_2$	1.360	1.415	1.419	1.419	-1.06	-1
3·$TCNQF_4$	1.355	1.408	1.417	1.416	-1.11	-1
	1.351	1.414	1.414	1.420	-0.98	-1
4·$TCNQF_4$	1.358	1.419	1.414	1.414	-0.98	-1
$(5)_2$·$TCNQF_4$	1.358	1.410	1.410	1.424	-0.92	-1

Table S4: Nitrile Frequencies in the $TCNQF_4$ of CT complexes.

Compound	V_{CN}(cm^{-1})	
$TCNQF_4$	2194	2227
1·$TCNQF_4$	2167	2190
2·$TCNQF_4$·($C_2H_4Cl_2$)	2169	2191
3·$TCNQF_4$	2171	2193
4·$TCNQF_4$	2168	2190
$(5)_2$·$TCNQF_4$	2170	2192

Crystal structures

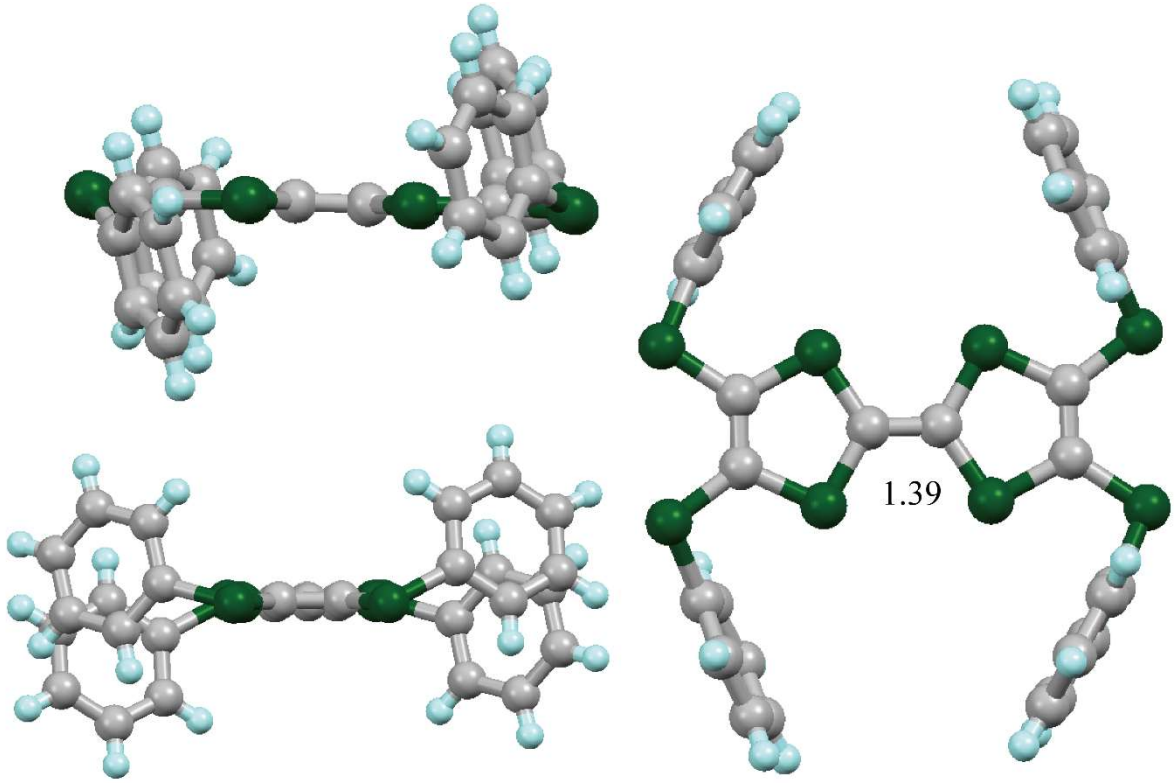


Figure S6: Molecular geometry of 1 in 1·$TCNQF_4$.

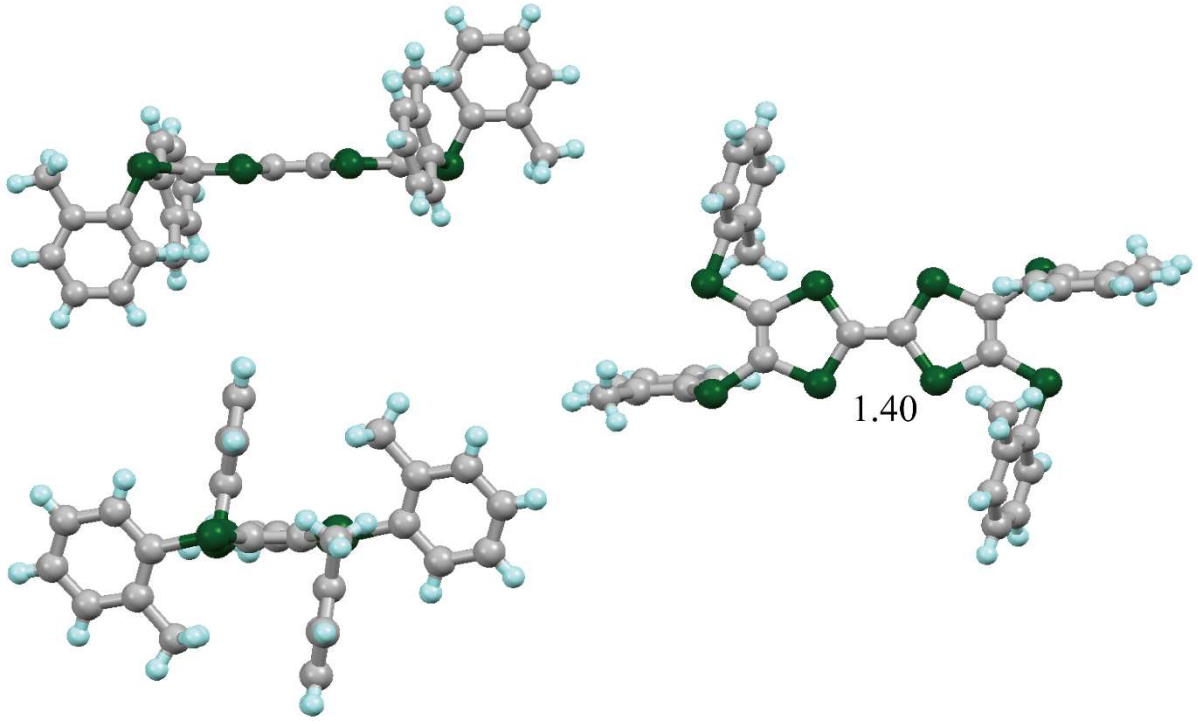


Figure S7: Molecular geometry of 2 in 2·$TCNQF_4$·$C_2H_4Cl_2$.

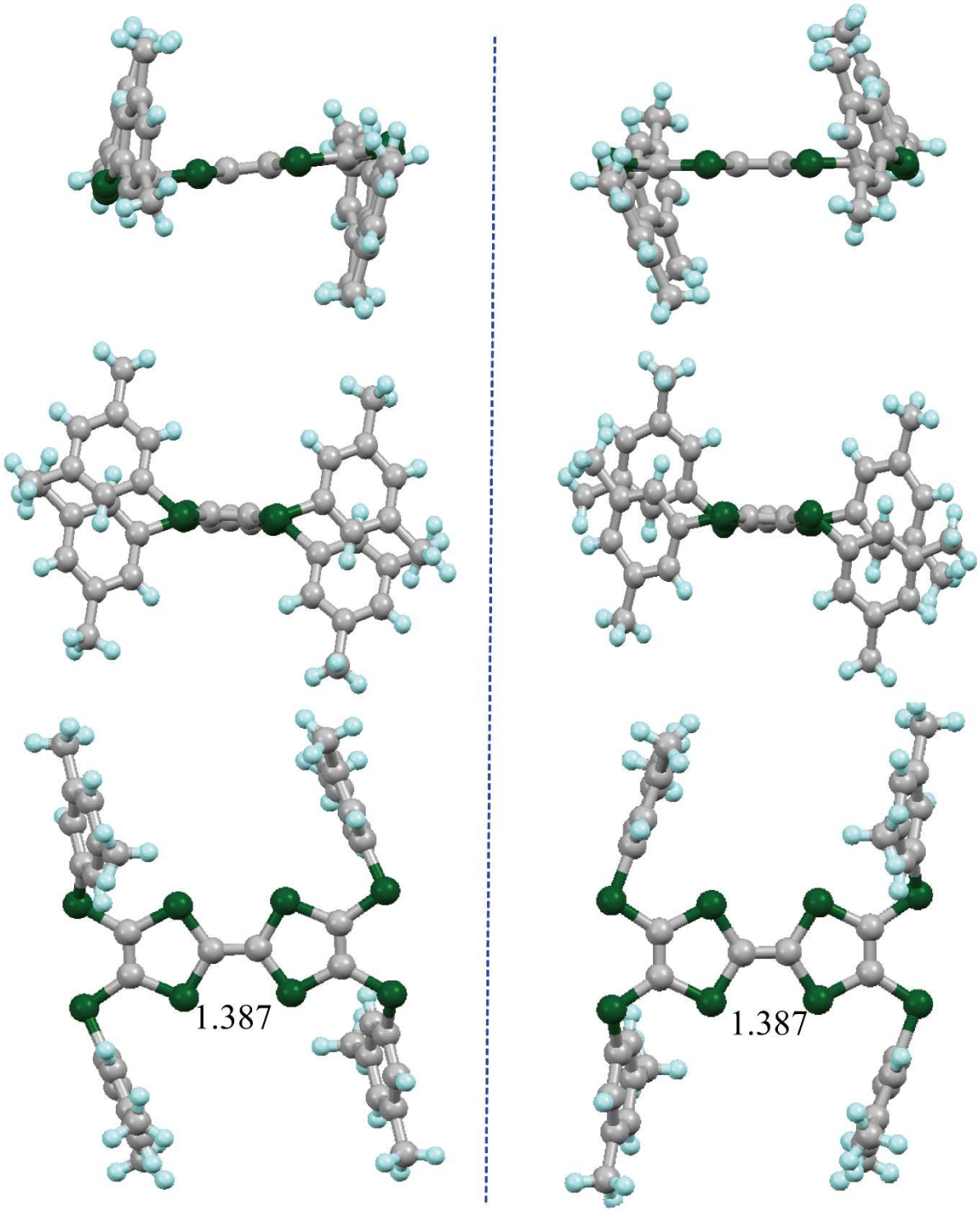


Figure S8: Molecular geometry of 3 in 3·$TCNQF_4$.

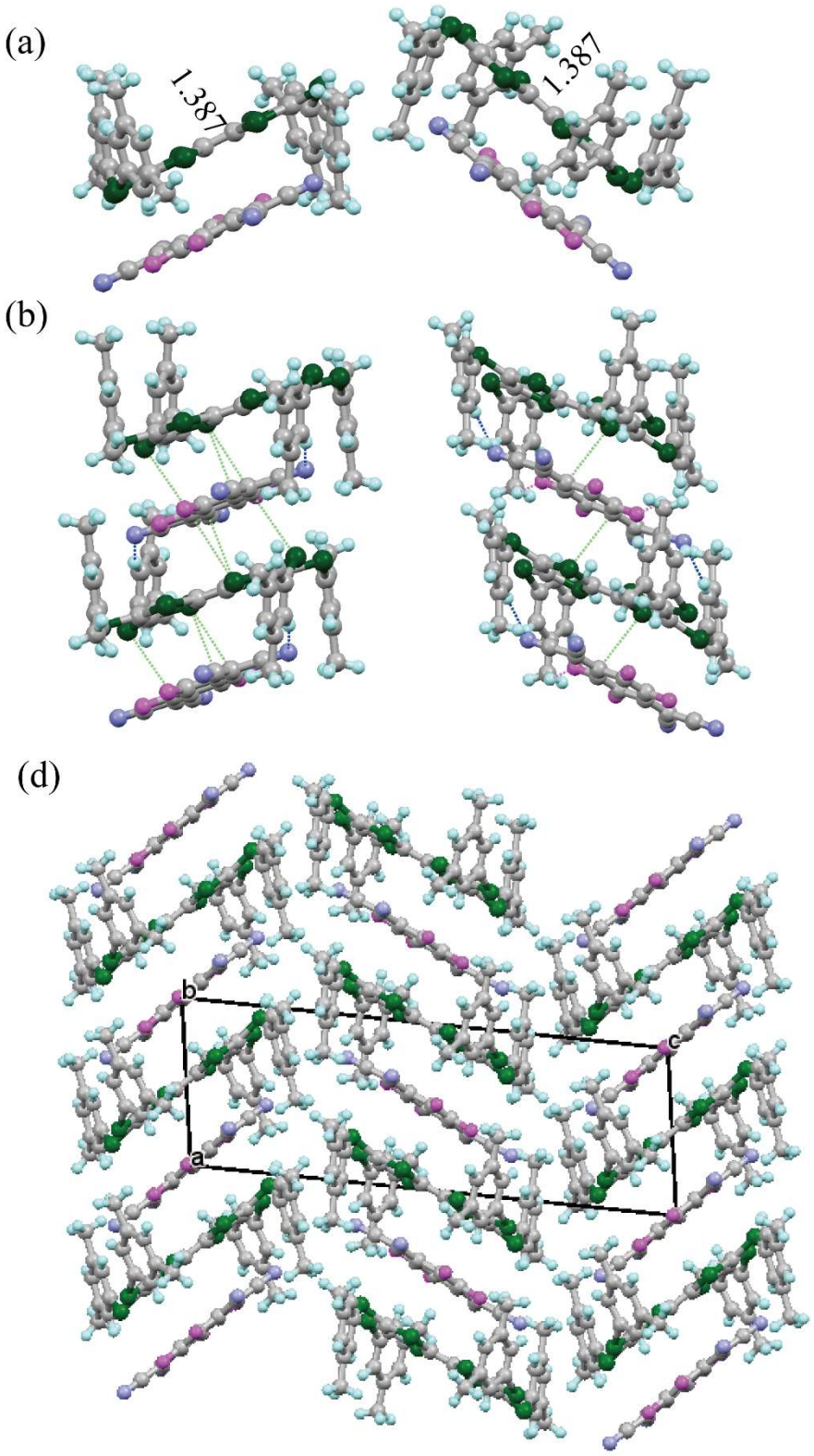


Figure S9: Crystal structure of 3·$TCNQF_4$: a) unit cell contents with the typical bond lengths shown (in Å); b) interactions between 3 and $TCNQF_4$; c) packing structure viewed along the *b*-axis.

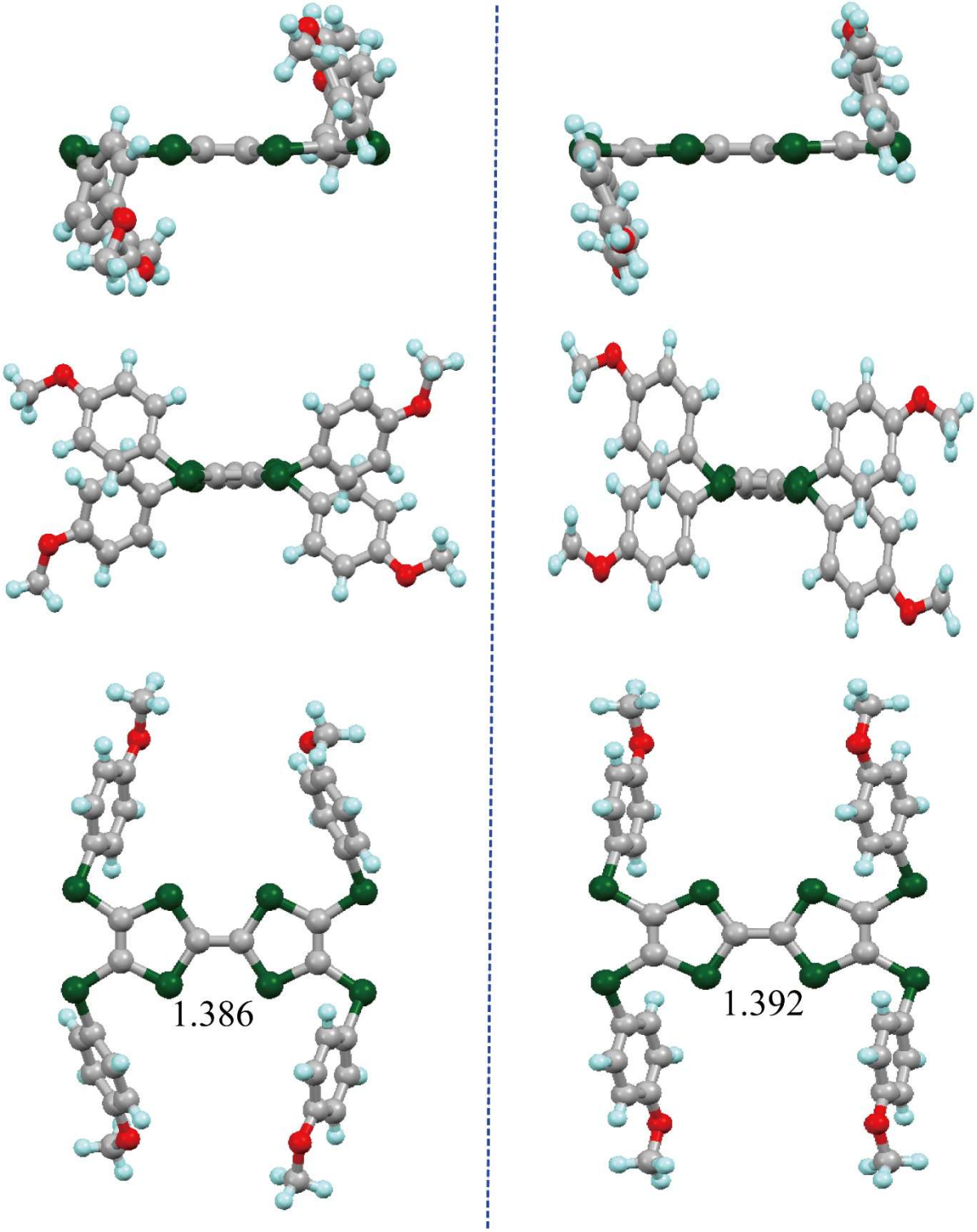


Figure S10: Molecular geometry of 4 in 4·$TCNQF_4$.

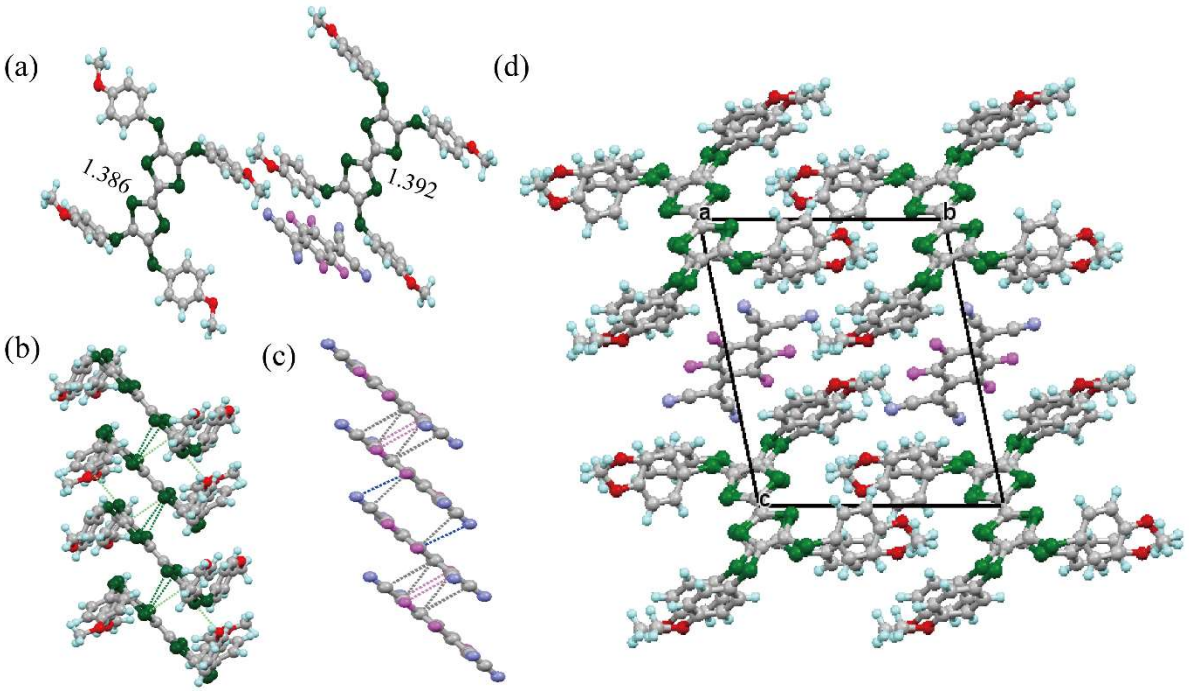


Figure S11: Crystal structure of 4·$TCNQF_4$: a) unit cell contents with the typical bond lengths shown (in Å); b) interactions between 4; c) interactions between $TCNQF_4$; d) packing structure viewed along the *a*-axis.

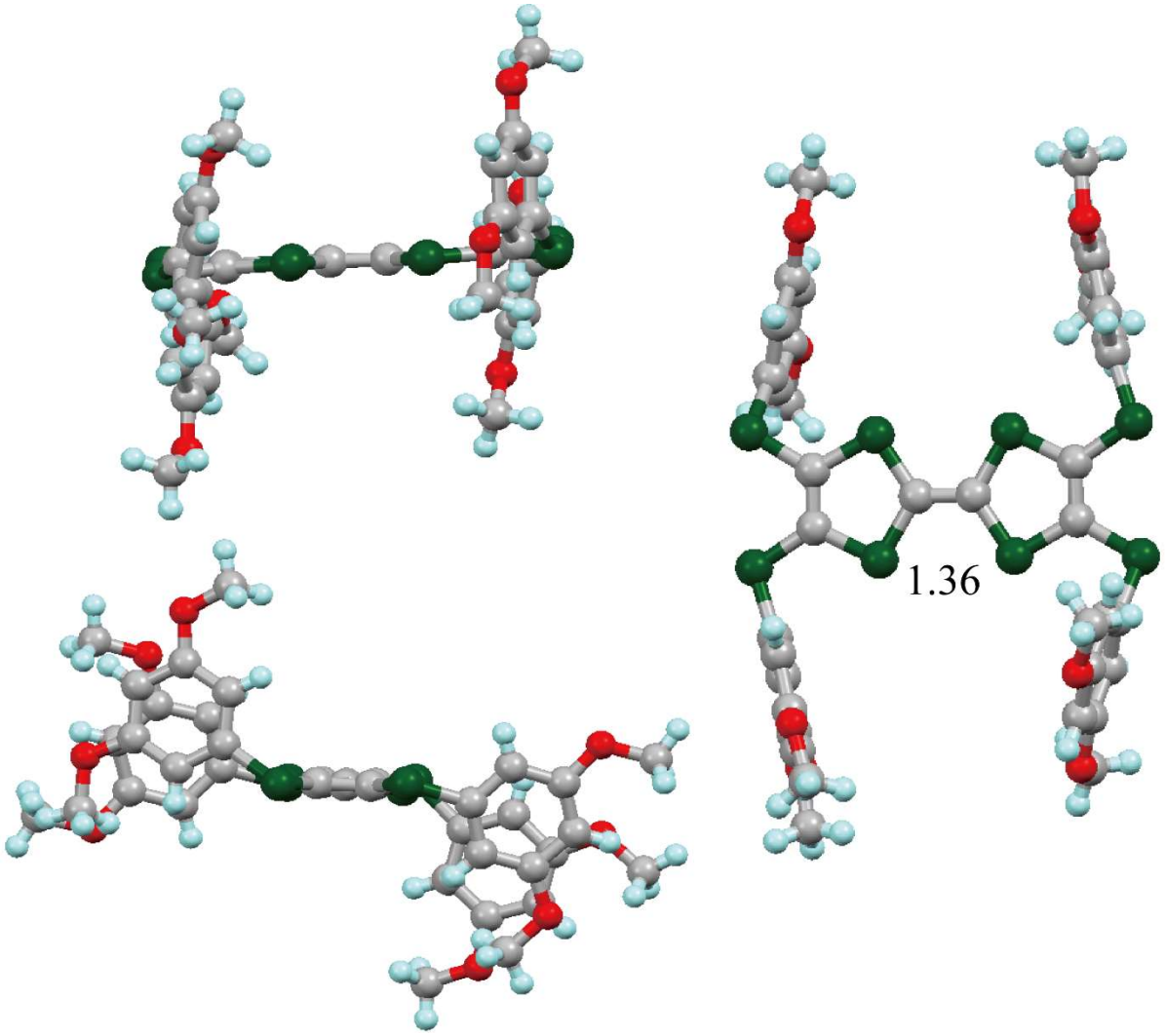


Figure S12: Molecular geometry of 5 in $(5)_2 \cdot TCNQF_4$.