Synthesis and Characterization of Charge Transfer Salts Based on [M(dcdmp)$_2$] (M=Au, Cu and Ni) with TTF type donors

Rafaela A. L. Silva, Isabel C. Santos, Sandra Rabaça, Elsa B. Lopes, Vasco Gama, Manuel Almeida and Dulce Belo *

C^{2}TN, Centro de Ciências e Tecnologias Nucleares, Instituto Superior Técnico, Universidade de Lisboa, E.N. 10 ao km 139.7, 2695-066 Bobadela LRS, Portugal; rafaela@ctn.tecnico.ulisboa.pt (R.A.L.S.); icsantos@ctn.tecnico.ulisboa.pt (I.C.S.); sandrar@ctn.tecnico.ulisboa.pt (S.R.); eblopes@ctn.tecnico.ulisboa.pt (E.B.L.); vascog@ctn.tecnico.ulisboa.pt (V.G.); malmeida@ctn.tecnico.ulisboa.pt (M.A.)

* Correspondence: dbelo@ctn.tecnico.ulisboa.pt; Tel.: +351-21-955-6203

Supplementary Materials

Table S1. Bond lengths of the donor and acceptor in the crystal structure of (α-DT-TTF)[Au(dcdmp)$_2$] (**1**).

(α-DT-TTF)$^+$	**d (Å)**	**[Au(dcdmp)$_2$]$^-$**	**d (Å)**
S5-C13	1.726(12)	Au1-S1	2.312(3)
S5-C15	1.718(13)	Au1-S2	2.307(3)
S6-C13	1.743(13)	Au1-S3	2.327(3)
S6-C14	1.719(12)	Au1-S4	2.318(3)
S8-C18	1.721(13)	S1-C1	1.750(12)
S8-C19	1.740(12)	S2-C2	1.734(11)
S9-C18	1.737(12)	S3-C7	1.735(13)
S9-C20	1.709(12)	S4-C8	1.725(11)
C13-C18	1.367(16)	N1-C1	1.325(16)
C14-C15	1.372(18)	N1-C3	1.348(16)
C14-S7	1.705(13)	N2-C2	1.330(13)
C15-C16	1.598(18)	N2-C4	1.337(19)
C17-H17	0.95	N3-C5	1.17(2)
C17-S7	1.668(16)	N4-C6	1.141(17)
C17-C16	1.46(2)	N5-C7	1.325(14)
C19-C20	1.38(2)	N5-C9	1.33(2)
C19-C21A	1.53(7)	N6-C8	1.324(16)
C19-S10	1.704(18)	N6-C10	1.343(16)
C20-C21	1.50(3)	N7-C11	1.150(17)
C20-S10A	1.690(17)	N8-C12	1.13(2)
C22-H22	0.95	C1-C2	1.408(17)
C22-S10	1.61(2)	C3-C4	1.381(18)
C22-C21	1.50(5)	C3-C5	1.43(2)

Table S1. Bond lengths of the donor and acceptor in the crystal structure of (α-DT-TTF)[Au(dcdmp)$_2$] (**1**). (cont.)

(α-DT-TTF)$^+$	**d (Å)**	**[Au(dcdmp)$_2$]$^-$**	**d (Å)**
C22-C21A	1.51(8)	C4-C6	1.446(18)
C22-S10A	1.56(2)	C7-C8	1.447(17)
C21-H21	0.95	C9-C10	1.386(19)
C21A-H21A	0.,95	C9-C11	1.441(18)
C16-H16	0.95	C10-C12	1.45(2)

Table S2. Short S···S and S···N contacts and hydrogen bonds in the crystal structure of (α-DT-TTF)[Au(dcdmp)$_2$] (**1**).

	Symm. op.*	**Length (Å)**	**Contact type**
S1···S2*	x,-1+y,z	3.537(5)	A-A M
S1···S4*	x,-1+y,z	3.550(5)	A-A M
S3···S4*	x,-1+y,z	3.553(5)	A-A M
S2···S10*	-1+x,1+y,z	3.70(1)	D-A M
S4···S8*	-1+x,1+y,z	3.555(5)	D-A M
N8···S5*	-1+x,1+y,z	3.15(1)	D-A M
N8···H16*-C16	-1+x,1+y,z	2.724 (119.6 °)	D-A M
S1···S6*	x,-1+y,z	3.661(4)	D-A M
S1···S9*	x,-1+y,z	3.598(5)	D-A M
S3···S6*	x,-1+y,z	3.641(5)	D-A M
S3···S7*	x,-1+y,z	3.654(5)	D-A M
N3···H21*-C21	x,-1+y,z	2.6 (158.61 °)	A-D L
N7···H17*-C17	-x,-1/2+y,1-z	2.523 (123.80 °)	A-D L
N7···S7*	-x,-1/2+y,1-z	3.30(1)	A-D L
N8···H17*-C17	-x,1/2+y,1-z	2.552(141.21 °)	A-D L
N3···H22*-C22	1-x,-1/2+y,-z	2.402 (143.03 °)	A-D L
N4···H22*-C22	1-x,1/2+y,-z	2.54 (126.12 °)	A-D L
N4···S10*	1-x,1/2+y,-z	3.36(2)	A-D L
S5···S6*	x,-1+y,z	3.675(4)	D-D M
S8···S6*	x,-1+y,z	3.680(5)	D-D M
S10···S9*	x,-1+y,z	3.61(1)	D-D M
S10A···N3*	x,y,z	3.29(2)	D-A M

M - Between stacks along the molecules minor axis; L - Between stacks along the molecules long axis.

Table S3. Bond lengths of the donor and acceptor in the crystal structure **2M** - (BET-TTF)[Au(dcdmp)$_2$].

(BET-TTF)$^+$	**d (Å)**
S5-C13	1.720(9)
S5-C15	1.742(9)
S6-C13	1.742(8)
S6-C14	1.736(9)
S7-C14	1.722(8)
S7-C17	1.805(9)
S8-C18	1.733(9)
S8-C20	1.733(8)
S9-C18	1.735(8)
S9-C19	1.730(9)
S10-C19	1.749(8)
S10-C22	1.827(9)
C13-C18	1.378(12)
C14-C15	1.347(11)
C15-C16	1.551(11)
C16-H16A	0.9900
C16-H16B	0.9900
C16-C17	1.598(10)
C17-H17A	0.9900
C17-H17B	0.9900
C19-C20	1.334(11)
C20-C21	1.560(12)
C21-H21A	0.9900
C21-H21B	0.9900
C21-C22	1.554(11)
C22-H22A	0.9900
C22-H22B	0.9900

[Au(dcdmp)$_2$]$^-$	**d (Å)**
Au1-S1	2.315(2)
Au1-S2	2.308(2)
Au1-S3	2.321(2)
Au1-S4	2.3133(19)
S1-C1	1.727(9)
S2-C2	1.742(8)
S3-C7	1.744(8)
S4-C8	1.739(8)
N1-C1	1.318(10)
N1-C3	1.344(11)
N2-C2	1.329(11)
N2-C4	1.337(10)
N3-C5	1.145(10)
N4-C6	1.141(11)
N5-C7	1.309(10)
N5-C9	1.346(10)
N6-C8	1.352(10)
N6-C10	1.330(10)
N7-C11	1.131(11)
N8-C12	1.146(10)
C1-C2	1.428(11)
C3-C4	1.381(11)
C3-C5	1.453(12)
C4-C6	1.469(14)
C7-C8	1.432(11)
C9-C10	1.391(11)
C9-C11	1.449(14)
C10-C12	1.459(12)

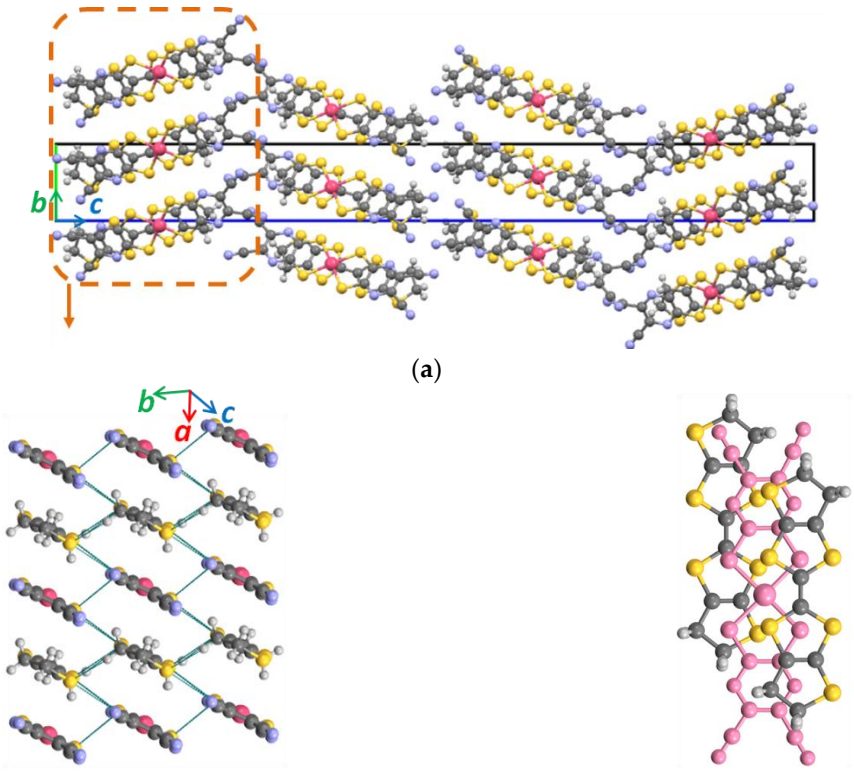


Figure S1. Crystal structure of (BET-TTF)[Au(dcdmp)$_2$] (**2M**): (**a**) view along the stacking axis; (**b**) partial view along the long axis of the molecules of neighbouring stacks in the same layer; (**c**) overlap mode of the mixed stacks. Thin lines represent relevant short contacts.

Table S4. Short S···S and S···N contacts and hydrogen bonds in the crystal structure **2M** - (BET-TTF)[Au(dcdmp)$_2$].

Structure M	Symm. op.*	Length (Å)	Contact type
S1···S2*	-1+x,y,z	3.613(3)	A-A M
S1···S4*	-1+x,y,z	3.588(3)	A-A M
S3···S4*	-1+x,y,z	3.594(3)	A-A M
S2···S7*	-1+x,y,z	3.661(3)	A-D M
S4···S6*	-1+x,y,z	3.567(2)	A-D M
N8···S8*	-1+x,y,z	3.183(8)	A-D M
S1···S5*	-1+x,1+y,z	3.584(2)	A-D M
S1···S9*	-1+x,1+y,z	3.663(3)	A-D M
S3···S9*	-1+x,1+y,z	3.609(3)	A-D M
S3···S10*	-1+x,1+y,z	3.576(3)	A-D M
N4···S7*	1-x,-1/2+y,1/2-z	3.359(9)	A-D L
N3···H17A*-C17	1-x,1/2+y,1/2-z	2.5 (129.98 °)	A-D L
N4···H16B*-C16	1-x,1.5+y,1/2-z	2.637 (144.43 °)	A-D L
N7···H21B*-C21	-1+x,-1/2-y,1/2+z	2.63 (147.20 °)	A-D L

M - Between stacks along the molecules minor axis; L - Between stacks along the molecules long axis.

Table S4. Short S···S and S···N contacts and hydrogen bonds in the crystal structure **2M** - (BET-TTF)[Au(dcdmp)$_2$]. (cont.)

Structure M	Symm. op.*	Length (Å)	Contact type
N7···S10*	-1+x,-1/2-y,1/2+z	3.32(1)	A-D L
S6···S9*	-1+x,1+y,z	3.683(3)	D-D M
S7···S5*	-1+x,1+y,z	3.578(3)	D-D M
S7···H16B*-C16	-1+x,1+y,z	2.95 (137.26 °)	D-D M
S8···S9*	-1+x,1+y,z	3.698(3)	D-D M
C21-H21B···S10*	-1+x,1+y,z	2.934 (138.89 °)	D-D M

M - Between stacks along the molecules minor axis; L - Between stacks along the molecules long axis.

Table S5. Bond lengths of the donor and acceptor in the crystal structure **2T** - (BET-TTF)[Au(dcdmp)$_2$].

(BET-TTF)$^+$	d (Å)
S3-C9	1.733(5)
S3-C7	1.736(5)
S4-C8	1.737(5)
S4-C7	1.739(5)
C7-C7	1.373(9)
C8-C9	1.336(7)
C8-C10A	1.51(4)
C8-S5	1.740(6)
C9-C10	1.498(12)
C9-S5A	1.782(11)
C11-C10	1.543(13)
C11-C10A	1.61(4)
C11-S5A	1.719(12)
C11-S5	1.810(6)
C11-H11A	0.9900
C11-H11B	0.9900
C10-H10A	0.9900
C10-H10B	0.9900
C10A-H10C	0.9900
C10A-H10D	0.9900

[Au(dcdmp)$_2$]$^-$	d (Å)
Au1-S1	2.3150(12)
Au1-S2	2.3176(11)
S1-C1	1.748(4)
S2-C2	1.732(5)
N1-C1	1.343(6)
N1-C3	1.348(5)
N2-C2	1.342(6)
N2-C4	1.356(6)
N3-C5	1.136(6)
N4-C6	1.133(6)
C1-C2	1.420(7)
C3-C4	1.377(7)
C3-C5	1.453(7)
C4-C6	1.447(6)

Table S6. Short S···S and S···N contacts and hydrogen bonds in the crystal structure **2T** - (BET-TTF)[Au(dcdmp)$_2$].

Structure T	Symm. op.*	Length (Å)	Contact type
S1···S2*	x,-1+y,z	3.659(1)	A-A M
S1···S1*	1-x,-y,-z	3.570(2)	A-A M
N3···H10C*-C10A	-x,1-y,-z	2.695 (125.75 °)	A-D Along the stack
S1···S4*	1-x,1-y,-z	3.527(2)	A-D M
N3···S5*	1+x,-1+y,z	3.177(4)	A-D M
N3···S3A*	x,-1+y,z	3.11(1)	A-D M
S2···S3*	1-x,1-y,-z	3.644(4)	A-D M
N4···S3*	1-x,1-y,1-z	3.349(7)	A-D L
S3A···S3A*	-x,1-y,1-z	3.690(4)	D-D L
S4···S4*	1-x,1-y,-z	3.607(2)	D-D M
S3···S5*	x,-1+y,z	3.651(4)	D-D M
S3···H10A*-C10	x,-1+y,z	2.947 (139.48°)	D-D M
C10A-H10C···S5*	x,-1+y,z	2.810 (141.05°)	D-D M
C10A-H10C···S3A*	x,-1+y,z	2.986 (152.57°)	D-D M

M - Between stacks along the molecules minor axis; L - Between stacks along the molecules long axis.

Table S7. Bond lengths of the donor and acceptor in the crystal structure of α-DT-TTF[Cu(dcdmp)$_2$] (**3**).

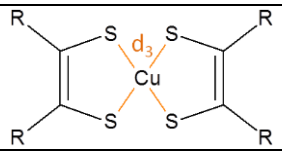
(α-DT-TTF)$^+$	d (Å)	[Cu(dcdmp)$_2$]$^-$	d (Å)
S5-C15	1.716(8)	Cu1-S1	2.184(2)
S5-C13	1.742(9)	Cu1-S2	2.184(3)
S6-C14	1.708(9)	Cu1-S3	2.179(3)
S6-C13	1.736(8)	Cu1-S4	2.187(3)
S8-C20	1.732(9)	S1-C1	1.719(9)
S8-C18	1.749(9)	S2-C2	1.725(8)
S9-C18	1.720(10)	S3-C7	1.712(8)
S9-C19	1.735(9)	S4-C8	1.744(9)
C13-C18	1.354(11)	N1-C3	1.334(11)
C14-C16A	1.33(3)	N1-C1	1.346(10)
C14-C15	1.383(11)	N2-C4	1.337(11)
C14-S7	1.738(9)	N2-C2	1.350(10)
C15-C16	1.44(3)	N3-C5	1.144(11)
C15-S7A	1.67(2)	N4-C6	1.130(11)
C17-C16	1.43(3)	N5-C7	1.323(10)
C17-S7A	1.56(2)	N5-C9	1.336(10)
C17-S7	1.628(12)	N6-C10	1.322(11)
C17-C16A	1.68(4)	N6-C8	1.335(10)
C17-H17	0.95	N7-C11	1.136(11)
C19-C20	1.364(12)	N8-C12	1.132(10)
C19-C21A	1.55(2)	C1-C2	1.405(12)

Table S7. Bond lengths of the donor and acceptor in the crystal structure of α-DT-TTF[Cu(dcdmp)$_2$] (**3**). (cont.)

(α-DT-TTF)$^+$	**d (Å)**
C19-S10	1.694(13)
C20-C21	1.53(2)
C20-S10A	1.637(17)
C22-C21	1.44(7)
C22-C21A	1.48(7)
C22-S10A	1.54(4)
C22-S10	1.573(17)
C22-H22	0.95
C16-H16	0.95
C16A-H16A	0.95
C21-H21	0.95
C21A-H21A	0.95

[Cu(dcdmp)$_2$]$^-$	**d (Å)**
C3-C4	1.411(12)
C3-C5	1.457(13)
C4-C6	1.451(12)
C7-C8	1.424(12)
C9-C10	1.376(12)
C9-C11	1.461(13)
C10-C12	1.464(12)

Table S8. Bond lengths of central Cu-S (d_3) bonds of [Cu(dcdmp)$_2$] units in the crystal structures of α-DT-TTF[Cu(dcdmp)$_2$] (**3**) and ET[Cu(dcdmp)$_2$] (**4**), compared with related compounds.

	**d_3 (Å)**				<d_3>
[Cu^{III}(mnt)$_2$]$^-$ [i]	2.184(2)	2.178(2)	2.184(2)	2.178(2)	2.181(2)
[Cu^{II}(dcdmp)$_2$]$^{2-}$ [ii]	2.2389(14)	2.2821(13)	2.2389(14)	2.2821(13)	2.2605(14)
α-DT-TTF[Cu(dcdmp)$_2$] (3)	2.184(2)	2.184(3)	2.179(3)	2.1873(6)	2.184(3)
(ET)[Cu(dcdmp)$_2$] (4)	2.1922(6)	2.1787(7)	2.1853(7)	2.1873(6)	2.1859(7)

[i] Ribas, X. *et al. Adv. Funct. Mater*. 2005, 15, 1023-1035.

[ii] Belo, D. *et al. Polyhedron* 2005, 24, 2035-2042.

Table S9. Short S···S and S···N contacts and hydrogen bonds in the crystal structure of α-DT-TTF[Cu(dcdmp)$_2$] (**3**).

	Symm. op.*	**Length (Å)**	**Contact type**
N7···H17*-C17	-1+x,y,z	2.554 (131.78°)	A-D L
S2···S6*	x,y,z	3.682(3)	A-D C
S2···S7*	x,y,z	3.594(6)	A-D C
S4···S6*	x,y,z	3.573(3)	A-D C
S1···S9*	-x,1/2+y,1/2-z	3.622(3)	A-D S
S3···S6*	-x,1/2+y,1/2-z	3.548(3)	A-D S
N4···H17*-C17	1-x,-1/2+y,1/2-z	2.615 (122.73°)	A-D L
N8···H22*-C22	-1-x,1-y,-z	2.519 (147.75°)	A-D L

C – Along the chain; S - Between chains in the same layer; L - Between chains in neighboring layers.

Table S9. Short S···S and S···N contacts and hydrogen bonds in the crystal structure of α-DT-TTF[Cu(dcdmp)$_2$] (**3**).

(cont.)

	Symm. op.*	Length (Å)	Contact type
S1···S5*	x,1.5-y,1/2+z	3.595(3)	A-D C
S1···S8*	x,1.5-y,1/2+z	3.568(3)	A-D C
S3···S8*	x,1.5-y,1/2+z	3.443(3)	A-D C
S3···H21*-C21	x,1.5-y,1/2+z	3.05 (124.59°)	A-D C
N3···H16*-C16	x,1.5-y,1/2+z	2.673 (163.43°)	A-D C
N5···H21*-C21	x,1.5-y,1/2+z	2.678 (160.96°)	A-D C
N3···H22*-C22	1+x,1.5-y,1/2+z	2.625 (123.25°)	A-D L
S5···S8*	-x,2-y,-z	3.625(3)	D-D S
N3*···S7A	x,1.5-y,1/2+z	3.34(2)	A-D C

C – Along the chain; S - Between chains in the same layer; L - Between chains in neighboring layers.

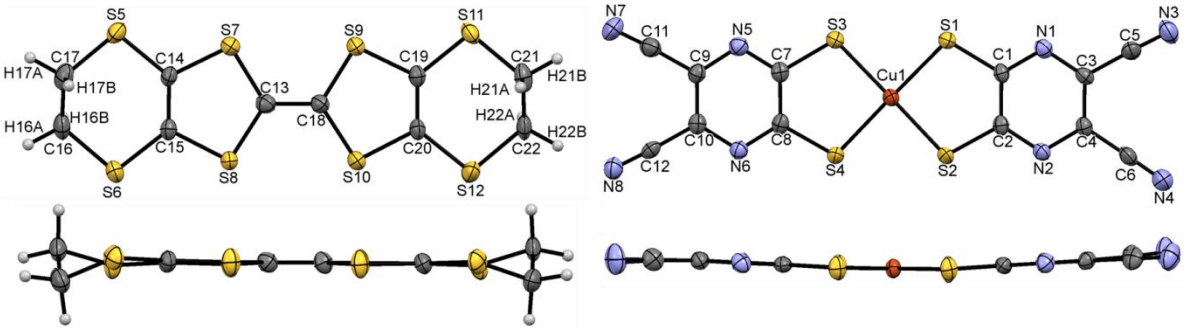


Figure S2. ORTEP and atomic numbering schemes (top and side views) of donor molecules and acceptor [Cu(dcdmp)$_2$] in the crystal structure of (**a**) ET[Cu(dcdmp)$_2$] (**4**), with thermal ellipsoids drawn at 70 % probability level.

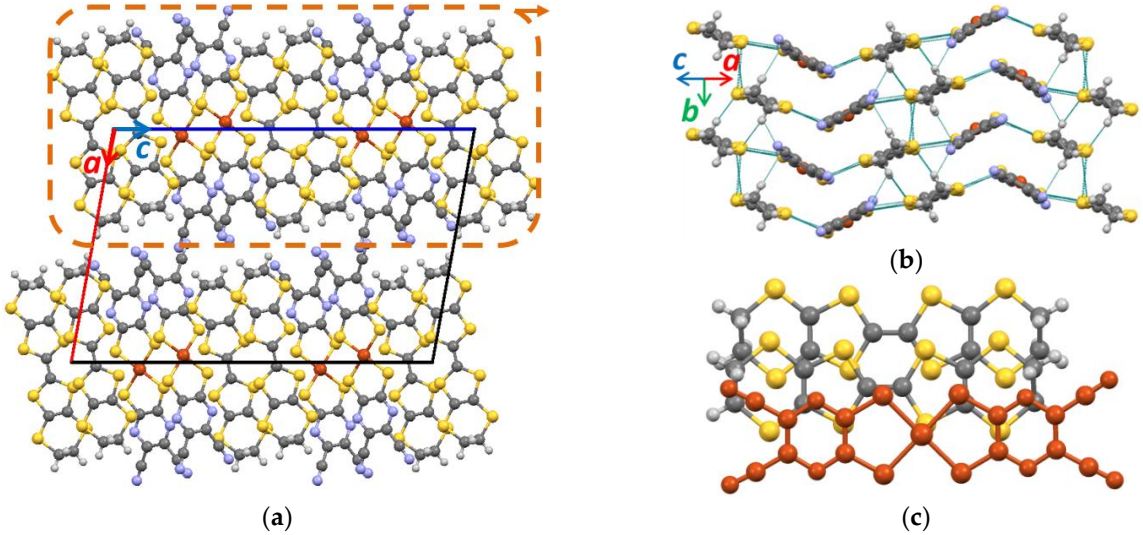


Figure S3. Crystal structure of (ET-TTF)[Cu(dcdmp)$_2$] (**4**): (**a**) view along the stacking axis; (**b**) partial view along the long axis of the molecules of neighbouring stacks in the same layer; (**c**) overlap mode of the mixed stacks. Thin lines represent relevant short contacts.

Table S10. Bond lengths of the donor and acceptor in the crystal structure of ET[Cu(dcdmp)$_2$] (**4**).

ET$^+$	**d (Å)**
S5-C14	1.737(3)
S5-C17	1.811(3)
S6-C15	1.740(2)
S6-C16	1.805(3)
S7-C13	1.718(3)
S7-C14	1.740(2)
S8-C13	1.723(2)
S8-C15	1.739(3)
S9-C18	1.727(2)
S9-C19	1.739(3)
S10-C18	1.721(3)
S10-C20	1.747(2)
S11-C19	1.739(2)
S11-C21	1.808(3)
S12-C20	1.738(3)
S12-C22	1.810(2)
C13-C18	1.385(3)
C14-C15	1.360(4)
C16-H16B	0.990
C16-H16A	0.989
C16-C17	1.520(4)
C17-H17B	0.991
C17-H17A	0.990
C19-C20	1.358(4)
C21-H21B	0.990
C21-H21A	0.989
C21-C22	1.522(4)
C22-H22B	0.990
C22-H22A	0.989

[Cu(dcdmp)$_2$]$^-$	**d (Å)**
Cu1-S1	2.1922(6)
Cu1-S2	2.1787(7)
Cu1-S3	2.1853(7)
Cu1-S4	2.1873(6)
S1-C1	1.726(3)
S2-C2	1.734(2)
S3-C7	1.738(2)
S4-C8	1.732(3)
N1-C1	1.336(3)
N1-C3	1.342(3)
N2-C2	1.323(3)
N2-C4	1.352(3)
N3-C5	1.144(3)
N4-C6	1.144(4)
N5-C7	1.327(4)
N5-C9	1.353(3)
N6-C8	1.332(3)
N6-C10	1.339(3)
N7-C11	1.143(4)
N8-C12	1.144(3)
C1-C2	1.427(4)
C3-C4	1.389(4)
C3-C5	1.452(3)
C4-C6	1.442(4)
C7-C8	1.424(4)
C9-C10	1.383(4)
C9-C11	1.448(4)
C10-C12	1.453(3)

Table S11. Short S···S and S···N contacts and hydrogen bonds in the crystal structure of (ET)[Cu(dcdmp)$_2$] (**4**).

	Symm. op.*	Length (Å)	Contact type
S2···S9*	x,y,z	3.5497(7)	D-A C
S2···S11*	x,y,z	3.448(1)	D-A C
S4···S7*	x,y,z	3.6547(9)	D-A C
N2···S11*	x,y,z	3.296(2)	D-A C
N8···S5*	x,y,z	3.255(3)	D-A C
N8···H21A*-C21	-x,1-y,-z	2.556 (168.80 °)	D-A L
N8···H22A*-C22	-x,2-y,-z	2.700 (120.84 °)	D-A S
C21-H21B···N3*	1-x,1/2+y,1/2-z	2.657 (127.02 °)	D-A L
C17-H17A···N7*	-1-x,1-y,-z	2.641 (144.83 °)	D-A L
C16-H16A···N4*	-1+x,1.5-y,-1/2+z	2.383 (154.33 °)	D-A L
S6···S3*	x,1.5-y,-1/2+z	3.684(1)	D-A C
S6···N5*	x,1.5-y,-1/2+z	3.275(2)	D-A C
S8···S3*	x,1.5-y,-1/2+z	3.6225(7)	D-A C
S12···N3*	x,1.5-y,-1/2+z	3.380(3)	D-A C
S5···S11*	-x,1-y,-z	3.5852(9)	D-D S
S7···S9*	-x,1-y,-z	3.6437(9)	D-D S
S5···H22A*-C22	-x,2-y,-z	2.8637 (148.84 °)	D-D S
S11···H16B*-C16	-x,2-y,-z	2.7522 (155.90 °)	D-D S
N2···H17B*-C17	-x,1-y,-z	2.767 (169.86 °)	D-A S

C – Along the chain; S - Between chains in the same layer; L - Between chains in neighboring layers.

Table S12. Bond lengths of the donor and acceptor in the crystal structure of (BET-TTF)$_2$[Cu(dcdmp)$_2$] (**5**).

(BET-TTF)$^+$	**d (Å)**	**(BET-TTF)$^+$**	**d (Å)**	**[Cu(dcdmp)$_2$]$^{2-}$**	**d (Å)**
S3-C8	1.710(4)	C7-C12	1.383(6)	Cu1-S1	2.2596(10)
S3-C7	1.715(4)	C13-C14	1.343(6)	Cu1-S2	2.2660(10)
S4-C9	1.717(4)	C13-C15A	1.61(2)	S1-C1	1.719(4)
S4-C7	1.734(4)	C13-S8	1.742(7)	S2-C2	1.715(4)
S6-C14	1.711(4)	C14-C15	1.467(16)	N1-C1	1.328(5)
S6-C12	1.727(4)	C14-S8A	1.715(5)	N1-C3	1.348(5)
S7-C13	1.714(4)	C16-C15	1.539(18)	N2-C4	1.337(5)
S7-C12	1.728(4)	C16-C15A	1.64(3)	N2-C2	1.342(5)
C11-C10A	1.527(13)	C16-S8	1.734(9)	N3-C5	1.141(5)
C11-C10	1.64(3)	C16-S8A	1.760(6)	N4-C6	1.133(6)
C11-S5	1.751(6)	C16-H16A	0.9900	C1-C2	1.444(5)

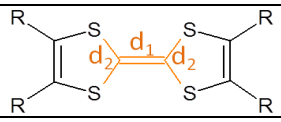
Table S12. Bond lengths of the donor and acceptor in the crystal structure of $(BET\text{-}TTF)_2[Cu(dcdmp)_2]$ (**5**). (cont.)

$(BET\text{-}TTF)^+$	**d (Å)**
C11-S5A	1.784(8)
C11-H11A	0.9900
C11-H11B	0.9900
C9-C8	1.340(6)
C9-C10	1.62(2)
C9-S5A	1.742(6)
C8-C10A	1.444(12)
C8-S5	1.751(5)

$(BET\text{-}TTF)^+$	**d (Å)**
C16-H16B	0.9900
C10-H10A	0.9900
C10-H10B	0.9900
C15-H15A	0.9900
C15-H15B	0.9900
C10A-H10C	0.9900
C10A-H10D	0.9900
C15A-H15C	0.9900
C15A-H15D	0.9900

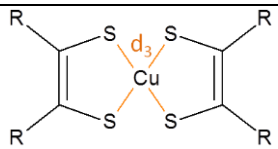
$[Cu(dcdmp)_2]^{2-}$	**d (Å)**
C3-C4	1.368(6)
C3-C5	1.440(6)
C4-C6	1.454(6)

Table S13. Bond lengths of central C=C (d_1) and central C-S (d_2) bonds of BET-TTF unit in the crystal structure of $(BET\text{-}TTF)_2[Cu(dcdmp)_2]$ (**5**) compared with related compounds.

	**d_1** (Å)	**d_2** (Å)				<d_2>
$(BET\text{-}TTF)^{\circ}$ [i]	1.360(4)	1.759(4)	1.759(4)	1.759(4)	1.759(4)	1.759(4)
$(BET\text{-}TTF)^{1/2+}$ [ii]	1.375(5)	1.738(2)	1.739(2)	1.735(2)	1.741(2)	1.738(2)
$(DT\text{-}TTF)^+$ [iii]	1.39(1)	1.717(8)	1.730(9)	1.717(8)	1.730(9)	1.724(9)
$(BET\text{-}TTF)_2[Cu(dcdmp)_2]$ (5)	1.392(3)	1.726(2)	1.725(2)	1.729(3)	1.728(2)	1.727(2)

[i] Rovira, C. *et al. J. Org. Chem.* **1994**, *59*, 3307-3313.
[ii] Tarrés, J. *et al. Chem. Mater.* **1995**, *7*, 1558-1567.
[iii] Ribas, X. *et al. Adv. Funct. Mater.* **2005**, *15*, 1023-1035.

Table S14. Bond lengths of central Cu-S (d_3) bonds of $[Cu(dcdmp)_2]$ units in the crystal structures of $(BET\text{-}TTF)_2[Cu(dcdmp)_2]$ (**5**), compared with related compounds.

	**d_3** (Å)				<d_3>
$[Cu^{III}(mnt)_2]^-$ [i]	2.184(2)	2.178(2)	2.184(2)	2.178(2)	2.181(2)
$[Cu^{II}(dcdmp)_2]^{2-}$ [ii]	2.2389(14)	2.2821(13)	2.2389(14)	2.2821(13)	2.2605(14)
$(BET\text{-}TTF)_2[Cu(dcdmp)_2]$ (5)	2.2596(10)	2.2660(10)	2.2596(10)	2.2660(10)	2.2628(10)

[i] Ribas, X. *et al. Adv. Funct. Mater.* **2005**, *15*, 1023-1035.
[ii] Belo, D. *et al. Polyhedron* **2005**, *24*, 2035-2042.

Table S15. Short S···S and S···N contacts and hydrogen bonds in the crystal structure of (BET-TTF)$_2$[Cu(dcdmp)$_2$] (**5**).

	Symm. op.*	Length (Å)	Contact type
S1···S7*	x,y,-1+z	3.373(1)	A-D C
S1···S8*	x,y,-1+z	3.501(7)	A-D C
N1···S8*	x,y,-1+z	3.252(7)	A-D C
S2···S3*	x,y,-1+z	3.564(1)	A-D C
S2···S7*	x,y,-1+z	3.675(1)	A-D C
N2···S3*	x,y,-1+z	3.380(3)	A-D C
N4···S5*	x,y,-1+z	3.381(5)	A-D C
S2···S4*	1-x,-y,-z	3.556(1)	A-D C
N4···H16B*-C16	x,y,-1+z	2.609 (133.98 °)	A-D L
N4···H11A*-C11	1-x,-y,-z	2.671 (313.93°)	A-D L
N2···H16A*-C16	x,y,-1+z	2.521 (150.98 °)	A-D M
S1···S3*	x,y,-1+z	3.687(2)	A-D M
N3···H11B*-C11	x,y,-1+z	2.572 (141.65 °)	A-D M
N3*···H11B-C11	-1-x,-y,2-z	2.832 (133.09 °)	A-D L
N3···N3*	1+x,y,-1+z	3.081(5)	A-A L
S3···S6*	1-x,-y,-z	3.445(2)	Between dimers
S4···S7*	1-x,-y,-z	3.451(2)	Between dimers
S5···H15B*-C15	1-x,-y,-z	3.027 (147.59 °)	Between dimers

C - Along the columns; M - Between stacks along the molecules minor axis; L - Between stacks along the molecules long axis.

Table S16. Bond lengths of the donor and acceptor in the crystal structure of ET$_2$[Ni(dcdmp)$_2$] (**6**).

ET^+	d (Å)	$[Ni(dcdmp)_2]^{2-}$	d (Å)
S3-C8	1.719(4)	Ni-S1	2.171
S3-C10	1.737(5)	Ni-S2	2.178
S8-C7	1.719(4)	S1-C1	1.723(5)
S8-C14	1.734(5)	S2-C2	1.718(5)
S9-C13	1.732(5)	C1-C2	1.439(7)
S9-C15	1.783(5)	C1-N1	1.329(6)
S4-C8	1.719(5)	C2-N2	1.335(6)
S4-C9	1.739(5)	N1-C3	1.349(6)
S5-C12	1.803(5)	N2-C4	1.354(6)
S5-C10	1.739(4)	C3-C4	1.373(7)
S10-C14	1.734(4)	C3-C5	1.441(7)
S10-C16	1.796(5)	C4-C6	1.445(7)

Table S17. Bond lengths of the donor and acceptor in the crystal structure of $ET_2[Ni(dcdmp)_2]$ (**6**). (cont.)

ET^+	d (Å)
S7-C7	1.724(5)
S7-C13	1.732(5)
S6-C9	1.740(5)
S6-C11	1.792(5)
C8-C7	1.381(6)
C14-C13	1.360(6)
C9-C10	1.356(6)
C12-H12A	0.969
C12-H12B	0.970
C12-C11	1.502(6)
C11-H11A	0.970
C11-H11B	0.970
C16-H16A	0.970
C16-H16B	0.971
C16-C15	1.492(8)
C15-H15A	0.970
C15-H15B	0.971

$[Ni(dcdmp)_2]^{2-}$	d (Å)
C5-N3	1.127(7)
C6-N4	1.127(7)

Table S17. Short S···S and S···N contacts and hydrogen bonds in the crystal structure of $(ET)_2[Ni(dcdmp)_2]$ (**6**).

	Symm. op.*	Length (Å)	Contact type
N4···H12B*-C12	x,y,z	2.737 (135.56°)	D-A L
S6···N3*	-x,-y,1-z	3.337(5)	D-A S
S3···S1*	x,1+y,z	3.603(2)	D-A C
S9···N4*	-x,1-y,-z	3.421(5)	D-A C
S5···S1*	x,1+y,z	3.477(2)	D-A C
S5···N1*	x,1+y,z	3.152(4)	D-A C
S7···S2*	-x,1-y,-z	3.583(2)	D-A C
C16-H16B···N3*	1+x,y,-1+z	2.516 (176.63°)	D-A L
S8···Ni*	1+x,y,z	3.387	D-A L
S9···H12B*-C12	-x,1-y,-z	3.028 (121.79°)	D-D L
S4···S10*	1-x,-y,-z	3.495(2)	D-D C
S10···S6*	1-x,-y,-z	3.384(2)	D-D C
S9···H11B*-C11	1-x,1-y,-z	2.889 (126.73°)	D-D L
S5···H16A*-C16	1-x,1-y,-z	2.971 (147.67°)	D-D L

C – Along the chain; S - Between chains in the same layer; L - Between chains in different layers.

EPR Measurements of $ET_2[Ni(dcdmp)_2]$ ***(6)***

EPR measurements performed at room temperature in a single crystal of compound **6** showed two lines: one narrow line ascribed to the ET^+ donor centered at g=2.0049 and a wider line at g=2.0182, that smoothly disappears as the temperature decreases (Figure S4). At 23 K this line is almost completely "diluted". This second line can be attributed to the paramagnetic impurities or to a partial oxidation of the $[Ni(dcdmp)_2]^{2-}$ specie, which suggests the possibility of different stoichiometries or phases in the same sample. Anisotropy studies were performed for the narrow line. The g values follow a sinusoidal behavior, both for horizontal and vertical rotation of the crystal, changing from 2.0037 to 2.017 and 2.00889 to 2.01758, respectively (Figure S5).

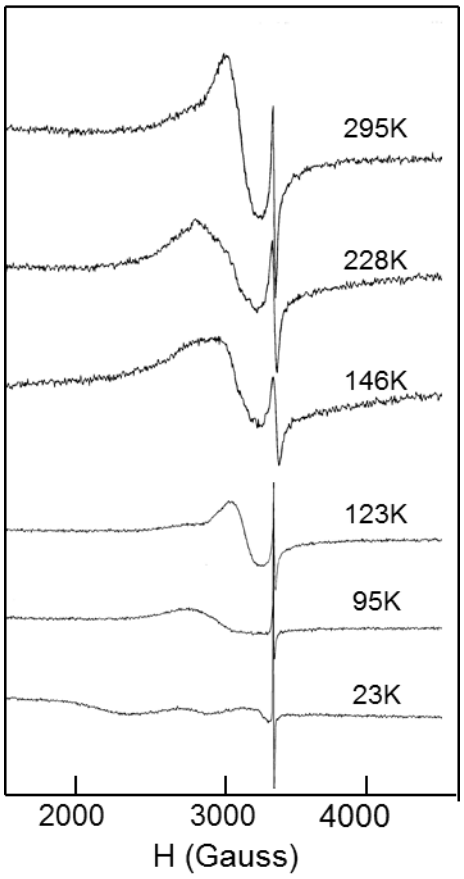


Figure S4. EPR spectra of $ET_2[Ni(dcdmp)_2]$ (**6**) at several temperatures.

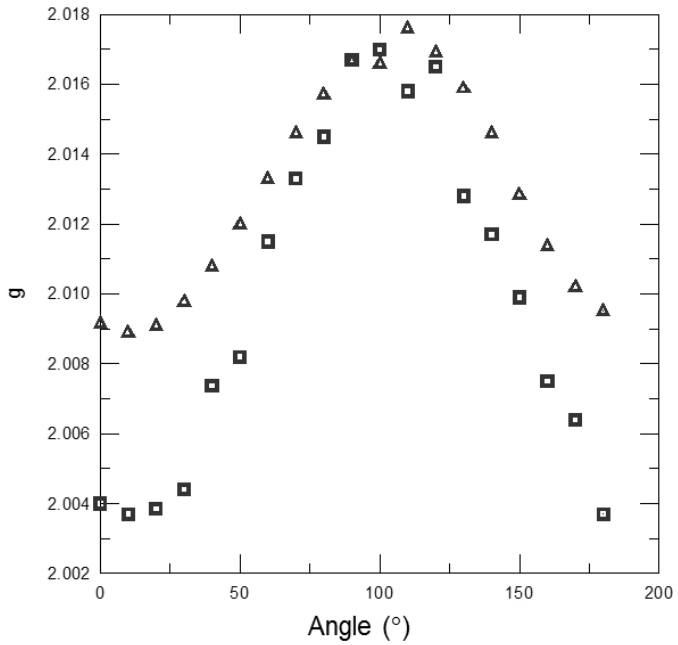


Figure S5. $ET_2[Ni(dcdmp)_2]$ (**6**) variation of g values in function of the angle of applied magnetic field: horizontal (square) and vertical (triangle) configurations.

Table S18. Donor bond lengths of α-mtdt in the crystal structure of (α-mtdt)$[Cu(dcdmp)_2]$ (**7**).

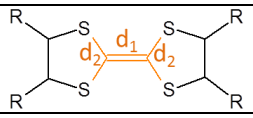
(α-mdtd)$^+$	**d (Å)**
S5-C15	1.703(9)
S5-C13	1.736(8)
S6-C13	1.728(9)
S6-C14	1.744(8)
S7-C15	1.733(8)
S7-C17	1.741(10)
S8-C19	1.717(8)
S8-C20	1.727(9)
S9-C19	1.713(9)
S9-C21	1.738(8)
S10-C20	1.772(8)
S10-C22	1.786(10)
S11-C21	1.739(10)
S11-C25	1.777(10)
N9-C24	1.248(14)
N10-C27	1.120(11)
C13-C19	1.406(11)
C14-C15	1.389(12)
C14-C16	1.506(12)
C16-C17	1.401(10)

(α-mdtd)$^+$	**d (Å)**
C16-H16	0.95
C17-C18	1.496(11)
C18-H18A	0.98
C18-H18B	0.98
C18-H18C	0.98
C20-C21	1.344(12)
C22-C23	1.41(2)
C22-H22A	0.99
C22-H22B	0.99
C23-C24	1.621(18)
C23-H23A	0.99
C23-H23B	0.99
C25-C26	1.517(11)
C25-H25A	0.99
C25-H25B	0.99
C26-C27	1.525(14)
C26-H26A	0.99
C26-H26B	0.99

Table S19. Bond lengths of [Cu(dcdmp)$_2$] molecules A and B in the crystal structure of (α-mtdt)[Cu(dcdmp)$_2$] (**7**).

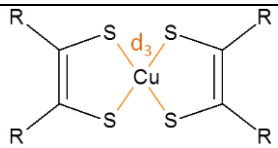
[Cu(dcdmp)$_2$]$^-$ –A–	**d (Å)**	**[Cu(dcdmp)$_2$]$^-$ –B–**	**d (Å)**
Cu1-S1	2.193(2)	Cu2-S3	2.1901(19)
Cu1-S2	2.179(3)	Cu2-S4	2.175(2)
S1-C1	1.714(9)	S3-C7	1.710(10)
S2-C2	1.730(8)	S4-C8	1.732(7)
N1-C1	1.327(9)	N5-C9	1.335(12)
N1-C3	1.357(12)	N5-C7	1.347(9)
N2-C2	1.330(11)	N6-C8	1.353(11)
N2-C4	1.334(10)	N6-C10	1.359(9)
N3-C5	1.151(10)	N7-C11	1.148(9)
N4-C6	1.166(13)	N8-C12	1.118(11)
C1-C2	1.439(13)	C7-C8	1.419(13)
C3-C4	1.370(13)	C9-C10	1.387(13)
C3-C5	1.450(12)	C9-C11	1.445(10)
C4-C6	1.466(15)	C10-C12	1.470(14)

Table S20. Bond lengths of central C=C (d_1) and central C-S (d_2) bonds of the pre-α-mtdt unit in the crystal structure of (α-mtdt)$_2$[Cu(dcdmp)$_2$] (**7**) and related compounds.

	**d_1**	**d_2**				<d_2 >
α-mtdt	1.36(3)	1.74(2)	1.75(2)	1.81(2)	1.75(2)	1.76 (2)
(α-mDT-TTF)[Co(mnt)$_2$] [i]	1.392(6)	1.731(5)	1.722(5)	1.723(5)	1.726(5)	1.726(5)
(α-mtdt)[Cu(dcdmp)$_2$] (7)	1.41(1)	1.713(9)	1.717(8)	1.728(9)	1.736(8)	1.724(8)

[i] Silva, R. A. L. *et al. Eur. J. Inorg. Chem.* **2015**, *30*, 5003-5010.

Table S21. Bond lengths of central Cu-S (d_3) bonds of [Cu(dcdmp)$_2$] units in the crystal structures of (α-mtdt)$_2$[Cu(dcdmp)$_2$] (**7**), compared with related compounds.

		**d_3** (Å)				<d_3>
[Cu^{III}(mnt)$_2$]$^-$ [i]		2.184(2)	2.178(2)	2.184(2)	2.178(2)	2.181(2)
[Cu^{II}(dcdmp)$_2$]$^{2-}$ [ii]		2.2389(14)	2.2821(13)	2.2389(14)	2.2821(13)	2.2605(14)
(α-mtdt)[Cu(dcdmp)$_2$] (7)	**A**	2.193(2)	2.179(3)	2.193(2)	2.179(3)	2.186(3)
	B	2.1901(19)	2.175(2)	2.1901(19)	2.175(2)	2.183(1)

[i] Ribas, X. *et al. Adv. Funct. Mater*. **2005**, *15*, 1023-1035.

[ii] Belo, D. *et al. Polyhedron* 2005, 24, 2035-2042.

Table S22. Short S···S contacts and hydrogen bonds in the crystal structure of (pre-α-mtdt)[Cu(dcdmp)$_2$] (**7**).

	Symm. op.*	Length (Å)	Contact type
S5···S11	1+x,y,z	3.675(3)	D-D Along the stack
S6···S10	1+x,y,z	3.586(3)	D-D Along the stack
N1···H16*-C16	x,y,1+z	2.676 (140.28)	A$_{mol\ A}$-D M
S2···S10*	1+x,y,1+z	3.588(4)	A$_{mol\ A}$-D M
S1···S8*	1+x,y,1+z	3.635(4)	A$_{mol\ A}$-D M
N3···H16*-C16	1+x,y,1+z	2.679 (115.10)	A$_{mol\ A}$-D M
N4···H25A*-C25	2+x,-1+y,1+z	2.598 (132.65)	A$_{mol\ A}$-D L
N8···S7*	-2+x,y,z	3.169(8)	A$_{mol\ B}$-D M
N6···S5*	-1+x,y,z	3.190(6)	A$_{mol\ B}$-D M
N6···S7*	-1+x,y,z	3.282(7)	A$_{mol\ B}$-D M
S4···S9*	x,y,z	3.646(3)	A$_{mol\ B}$-D M
S3···H25A*-C25	1+x,y,z	3.009 (138.44)	A$_{mol\ B}$-D M
N5···H25A*-C25	1+x,y,z	2.686 (128.90)	A$_{mol\ B}$-D M
N10···H22B*-C22	-x,2-y,-z	2.675 (125.46)	D-D L
N9···H23B*-C23	1-x,2-y,-z	2.372 (119.10)	D-D L
S7···H18A*-C18	3-x,1-y,1-z	2.85 (173.56)	D-D L

M - Between stacks along the molecules minor axis; L - Between stacks along the molecules long axis.

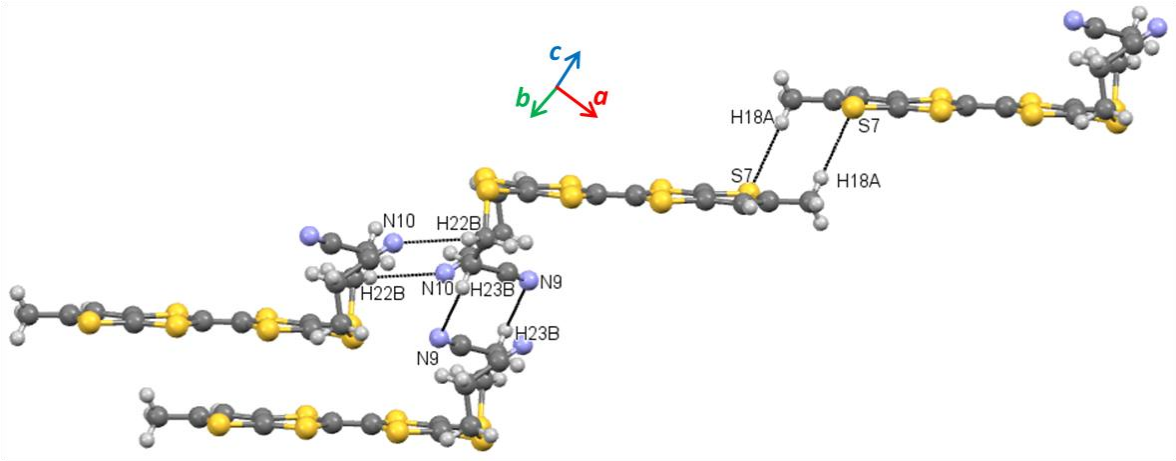


Figure S6. Detail showing the relevant short contacts between methyl and cyanoethyl groups of α-mtdt molecules in the crystal structure of (α-mtdt)[Cu(dcdmp)$_2$] (**7**).

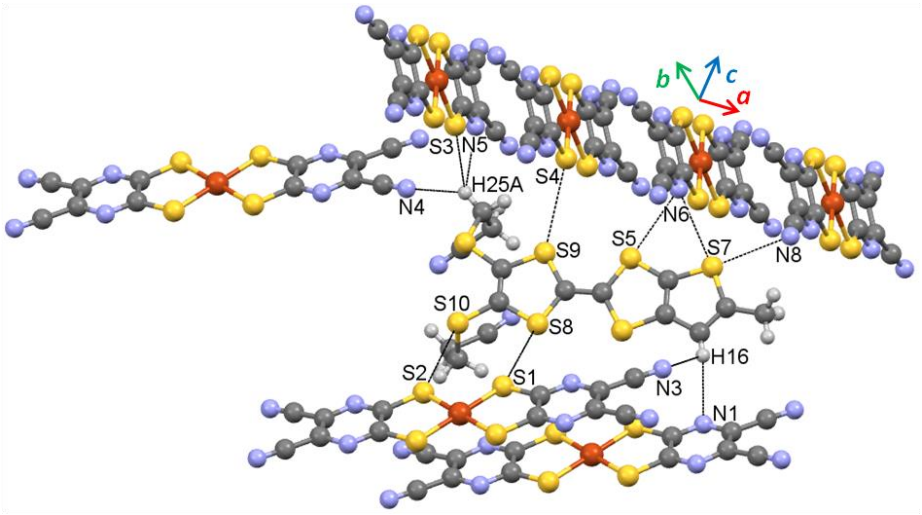


Figure S7. Detail showing the relevant short contacts between a α-mtdt molecule and different acceptors in the crystal structure of (α-mtdt)[Cu(dcdmp)$_2$] (**7**).