

Multistability in a family of DT-TTF organic radical based compounds (DT- TTF)₄[M(L)₂]₃ (M = Au, Cu; L = pds, pdt, bdt)

*João C. Dias, Xavi Ribas, Jorge Morgado, João Seiça, Elsa B. Lopes, Isabel C. Santos,
Rui T. Henriques, Manuel Almeida, Klaus Wurst, Pascale Foury-Leylekian, Enric
Canadell, José Vidal-Gancedo, Jaume Veciana, and Concepció Rovira*

Table S1. Short contact distances [Å] for (DT-TTF)₄[Au(pds)₂]₃ (**1**).

Atoms	distance	Atoms	distance
between [Au(pds)₂] and DT-TTF units			
Au1-S2 ^a	3.571(6)	Au2-S3 ^c	3.810(5)
Au1-S7 ^b	3.401(6)	Au2-S3 ^d	3.810(5)
Se1-S4 ^b	3.537(5)	Se1-S1 ^b	3.675(5)
Se2-S11 ^a	3.535(6)	Se2-S8 ^a	3.678(6)
Se3-S8 ^a	3.554(6)	Se4-S1 ^b	3.589(5)
Se4-S4 ^c	3.691(5)	Se5-S3 ^d	3.589(5)
Between DT-TTF units.			
	intra tetrads		inter tetrads
S1-S7 ^a	3.465(7)	S1-S1	4.001(7) ^f
S2-S8 ^a	3.597(8)	S1-S4	3.826(7) ^f
S4-S10 ^a	3.457(7)	S2-S2	4.133(8) ^b
S5-S11 ^a	3.595(8)	S2-S5	4.119(8) ^b
S7-S10 ^e	3.682(8)		

Symmetry operations: ^ax,y,z; ^b-1+x,y,z; ^c1-x,-y,1-z; ^d-1+x,y,-1+z; ^e2-x,1-y,1-z; ^f2-x,-y,1-z;

Table S2. Selected bond distances [Å] in the transition metal complex for compounds **1**, **3-4**.

Atoms	distance	Atoms	distance
(DT-TTF)₄[Au(pds)₂]₃ (1)			
AuSeComplex1			
Au1-Se1	2.4153(19)	Se1-C1	1.866(18)
Au1-Se2	2.4210(19)	Se2-C2	1.902(17)
Au1-Se3	2.4354(19)	Se3-C6	1.872(16)
Au1-Se4	2.425(2)	Se4-C5	1.913(16)
C1-C2	1.38(2)	C5-C6	1.40(2)
AuSeComplex2			
Au2-Se5	2.431(2)	Se5-C10	1.913(16)
Au2-Se6	2.427(3)	Se6-C9	1.924(17)
C9-C10	1.40(3)		
(DT-TTF)₄[Cu(pds)₂]₃ (3)			
CuSeComplex1		CuSeComplex2	
Cu1-Se1	2.292(2)	Cu2-Se5	2.306(2)
Cu1-Se2	2.295(2)	Cu2-Se6	2.302(2)
Cu1-Se3	2.296(2)	Cu2-Se7	2.297(2)
Cu1-Se4	2.309(2)	Cu2-Se8	2.294(2)
Se1-C1	1.920(15)	Se5-C9	1.912(14)
Se2-C2	1.894(13)	Se6-C10	1.898(13)
Se3-C5	1.900(13)	Se7-C13	1.884(13)
Se4-C6	1.889(14)	Se8-C14	1.877(14)
C1-C2	1.329(18)	C9-C10	1.332(17)
C5-C6	1.384(18)	C13-C14	1.398(18)
CuSeComplex3			
Cu3-Se9	2.302(2)	Se9-C17	1.892(15)
Cu3-Se10	2.309(3)	Se10-C18	1.924(15)
Cu3-Se11	2.293(2)	Se11-C21	1.892(14)
Cu3-Se12	2.291(2)	Se12-C22	1.817(16)
C17-C18	1.339(18)	C21-C22	1.413(19)
(DT-TTF)₄[Cu(pdt)₂]₃ (4)			
CuSComplex1		CuSComplex2	
Cu1-S25	2.180(2)	Cu2-S29	2.197(2)
Cu1-S26	2.181(2)	Cu2-S30	2.183(2)
Cu1-S27	2.181(2)	Cu2-S31	2.187(2)
Cu1-S28	2.188(2)	Cu2-S32	2.179(2)
S25-C1	1.738(8)	S29-C9	1.754(7)
S26-C2	1.751(7)	S30-C10	1.732(7)
S27-C5	1.734(8)	S31-C13	1.734(8)

S28-C6	1.756(8)	S32-C14	1.731(7)
C1-C2	1.385(10)	C9-C10	1.380(10)
C5-C6	1.415(10)	C13-C14	1.403(10)

CuSComplex3

Cu3-S33	2.180(2)	S33-C17	1.749(8)
Cu3-S34	2.191(2)	S34-C18	1.742(9)
Cu3-S35	2.180(2)	S35-C21	1.753(9)
Cu3-S36	2.175(2)	S36-C22	1.729(10)
C17-C18	1.418(11)	C21-C22	1.435(12)

Table S3. Short contact distances [Å] for (DT-TTF)₄[Cu(pds)₂]₃ (**3**).

Atoms	distance	Atoms	distance
Between Cu(pds)₂ and DT-TTF units			
DT1-CuSeComplex1		DT3-CuSeComplex2	
S6-Cu1 [*]	3.558	S13-Cu2	3.378
S1-Se1	3.531	S13-Se5	3.926
S4-Se1	3.632	S13-Se7	3.859
S4-Se3	3.458	S16-Se7	3.918
S3-Se1 [*]	3.884	S15-Se5 [*]	3.508
S6-Se1 [*]	3.836	S15-Se7 [*]	3.562
S6-Se3 [*]	3.904	S18-Se7 [*]	3.493
S-Se _{average}	3.708	S-Se _{average}	3.711
DT1-CuSeComplex2		DT4-CuSeComplex2	
S1-Se6	3.624	S19-Se6	3.503
S3-Se6	3.878	S19-Se8	3.635
S4-Se8	3.669	S22-Se8	3.542
S6-Se8	3.891	S21-Se6 [*]	3.810
S-Se _{average}	3.766	S24-Se8 [*]	3.832
		S-Se _{average}	3.664
		S21-Cu2 [*]	3.441
DT1-CuSeComplex3		DT4-CuSeComplex3	
S5-Cu3	3.628	S20-Cu3	3.8420
S5-Se9	3.743	S20-Se11	3.651
S5-Se10	3.683	S20-Se12	3.769
S2-Se9 [*]	3.720	S23-Se11 [*]	3.905
S-Se _{average}	3.715	S23-Se12 ^{**}	3.661
DT2-CuSeComplex1		S-Se _{average} 3.747	
S10-Cu1	3.312	DT4-CuSeComplex1	
S7-Se2	3.877	S19-Se1	3.810
S10-Se2	3.868	S21-Se1	3.721
S10-Se4	3.935	S22-Se3	3.740
S9-Se2 [*]	3.524	S24-Se3	3.744
S12-Se2 [*]	3.575	S-Se _{average}	3.754
S12-Se4 [*]	3.462		
S-Se _{average}	3.707		

Between DT-TTF units.

intra tetrads (DT1-DT2)		intra tetrads (DT3-DT4)	
S1-S7 ^a	3.378	S13-S19	3.752
S2-S8 ^a	3.799	S14-S20	3.892
S3-S9 ^e	3.489	S15-S19	3.794
S4-S10 ^a	3.386	S15-S21	3.599
S5-S11 ^a	3.825	S16-S22	3.728
S6-S12	3.516	S17-S23	3.783
S-S _{average}	3.566	S18-S24	3.582
		S-S _{average}	3.733

intra tetrads (DT2-DT3)		inter tetrads (DT4-DT1*)	
S7-S13	3.783	S24-S6	3.907
S7-S15	3.744	S21-S3	3.943
S8-S14	3.894		
S9-S15	3.795	S22-S4	3.803
S10-S16	3.768	S19-S1	3.808
S10-S18	3.747		
S11-S17	3.859		
S12-S18	3.768		
S-S _{average}	3.795		

Symmetry operations: ^ax,y,z; ^b-1+x,y,z; ^c1-x,-y,1-z; ^d-1+x,y,-1+z; ^e2-x,1-y,1-z; ^f2-x,-y,1-z;

Table S4. Short contact distances [\AA] for $(\text{DT-TTF})_4[\text{Cu}(\text{pdt})_2]_3$ (**4**).

Atoms	distance	Atoms	distance
Between $\text{Cu}(\text{pdt})_2$ and DT-TTF units			
DT1-CuSComplex1		DT3-CuSComplex2	
S6-Cu1*	3.498	S13-Cu2	3.373
S1-S25	3.486	S13-S29	3.840
S4-S25	3.543	S13-S31	3.752
S4-S27	3.366	S16-S31	3.878
S3-S25*	3.838	S15-S29*	3.413
S6-S25*	3.794	S15-S31*	3.496
S6-S27*	3.803	S18-S31*	3.482
S-S _{average}	3.638	S-S _{average}	3.644
DT1-CuSComplex2		DT4-CuSComplex2	
S1-S30	3.601	S19-S30	3.427
S3-S30	3.849	S19-S32	3.570
S4-S32	3.648	S22-S32	3.525
S6-S32	3.850	S21-S30*	3.707
S-S _{average}	3.737	S24-S32*	3.777
		S-S _{average}	3.601
		S21-Cu2*	3.431
DT1-CuSComplex3		DT4-CuSComplex3	
S5-Cu3	3.569	S20-Cu3	3.728
S5-S33	3.678	S20-S35	3.583
S5-S34	3.613	S20-S36	3.700
S2-S33*	3.634	S23-S35*	3.882
S-S _{average}	3.642	S23-S36**	3.579
DT2-CuSComplex1		S-S _{average} 3.687	
S10-Cu1	3.275	DT4-CuSComplex1	
S7-S26	3.884	S19-S25	3.805
S10-S26	3.802	S21-S25	3.664
S10-S28	3.853	S22-S27	3.739
S9-S26*	3.460	S24-S27	3.682
S12-S26*	3.465	S-S _{average}	3.723
S12-S28*	3.368		
S-S _{average}	3.639		

Between DT-TTF units.

intra tetrads (DT1-DT2)		intra tetrads (DT3-DT4)	
S1-S7 ^a	3.351	S13-S19	3.785
S2-S8 ^a	3.776	S14-S20	3.863
S3-S9 ^e	3.508	S15-S19	3.793
S4-S10 ^a	3.364	S15-S21	3.585
S5-S11 ^a	3.784	S16-S22	3.757
S6-S12	3.531	S17-S23	3.738
S-S _{average}	3.552	S18-S24	3.566
		S-S _{average}	3.727
intra tetrads (DT2-DT3)		inter tetrads (DT4-DT1*)	
S7-S13	3.736	S24-S6	3.790
S7-S15	3.721	S21-S3	3.827
S8-S14	3.868	S22-S4	3.685
S9-S15	3.745	S19-S1	3.679
S10-S16	3.702		
S10-S18	3.724		
S11-S17	3.807		
S12-S18	3.724		
S-S _{average}	3.753		

Symmetry operations: ^ax,y,z; ^b-1+x,y,z; ^c1-x,-y,1-z; ^d-1+x,y,-1+z; ^e2-x,1-y,1-z; ^f2-x,-y,1-z;

Structural description of compound DT-TTF(Cu(pdt)₂) (5)

Compound **5** crystallizes as dark-pink shining plates and was obtained under the same conditions as **4**, and usually each crystallization batch yielded a mixture of both. It crystallizes in the monoclinic system, space group $P2_1/n$ ($T = 233$ K), with an asymmetric unit containing one independent DT-TTF unit and one Cu(pdt)_2 molecule in general positions (see Figure S1). This 1:1 stoichiometric salt is characterized by the dimerization of both the DT-TTF units and the Cu(pdt)_2 units, in such a way that alternated layers of anions and cations are formed along b axis. The dimers alternate along a axis, allowing the formation chains of alternate dimers of anions and cations (see Figure S2). At the same time, each of these chains is surrounded by two parallel and four orthogonal chains, in a very similar way as the molecular packing found for neutral BEDT-TTF and ETEDT-TTF molecules.^{1,2} Each DT-TTF molecule supports one positive charge, which is in line with the longer central C=C distance of 1.387(9) Å.^{3d,4} The dimerization of the DT-TTF units and also of the Cu(pdt)_2 units is very strong, with interplanar distances of 3.519 Å and 3.589 Å, respectively. Indeed, four short S⋯S contacts exist between 3.40-3.42 Å in the perfectly overlapped DT-TTF dimers, whereas for the Cu(pdt)_2 dimers, the S⋯S contact are above 3.9 Å due to the lateral offset values of ca. 1.3 Å for the long axis of the skewed complexes. The chains are formed through short interdimer S⋯S contacts ranging between 3.38 and 3.61 Å. Finally, parallel chains are connected by aromatic π -stacking between the dithiophene rings of the DT-TTF and also between the pyrazine rings of the complexes. Only minor contacts are observed between perpendicular chains, i.e. one S⋯S contact of 3.64 Å between perpendicular DT-TTF dimers, and C-H⋯ π interactions between perpendicular complex dimers.

Figure S1. ORTEP for compound DT-TTF(Cu(pdt)₂) (**5**).

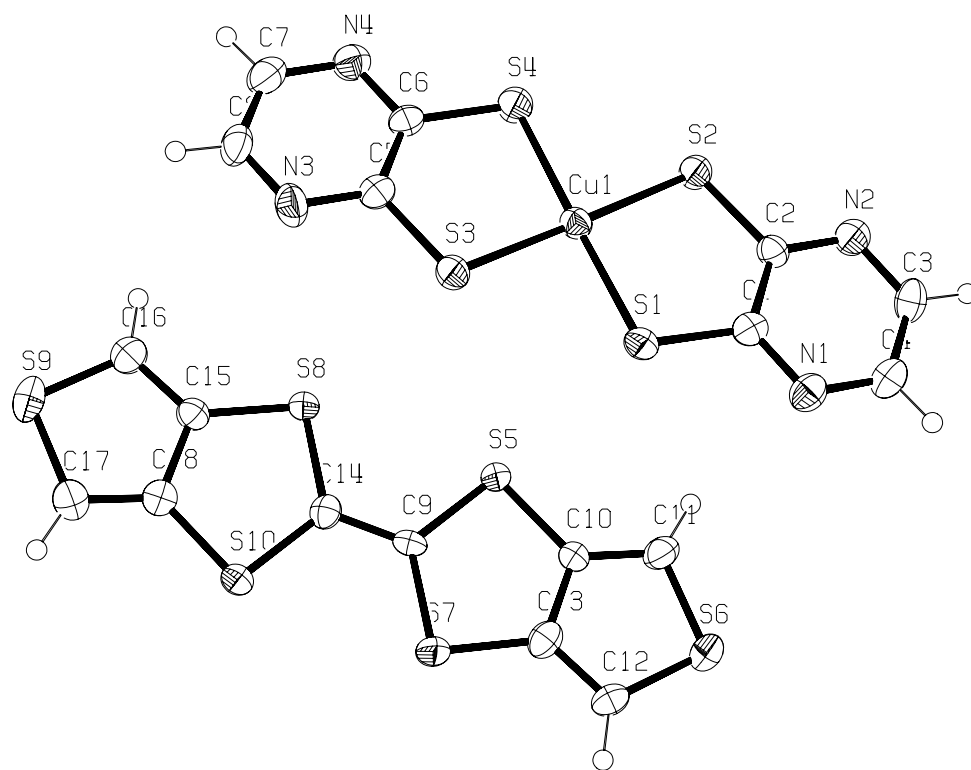
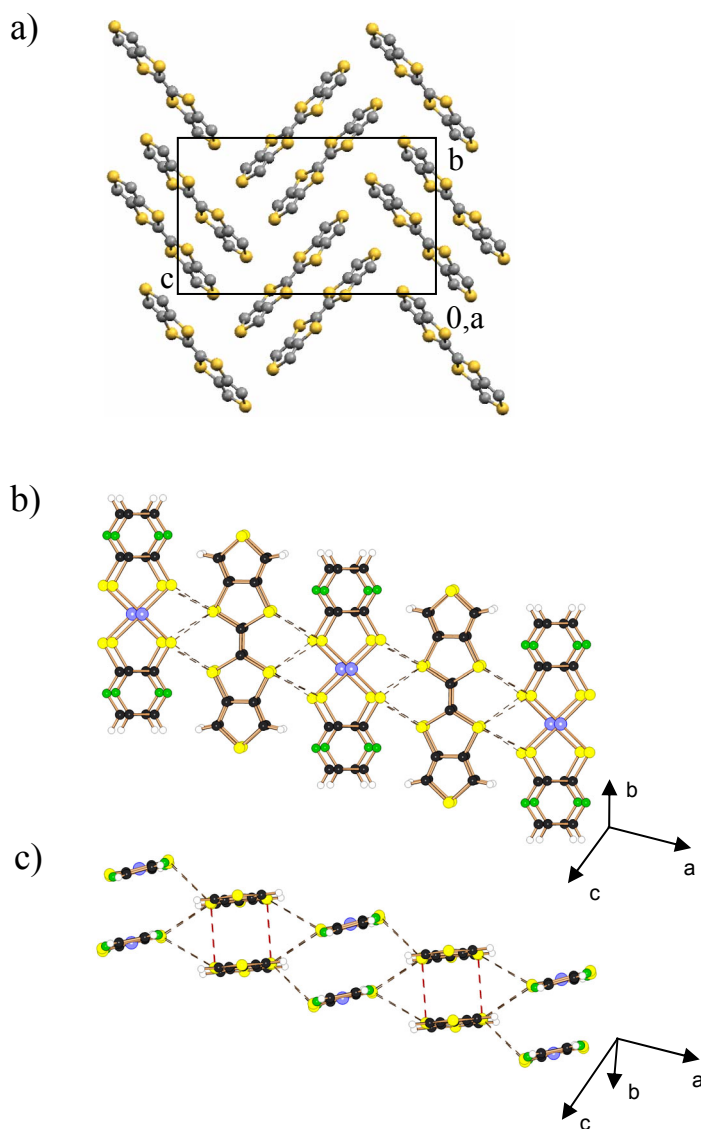


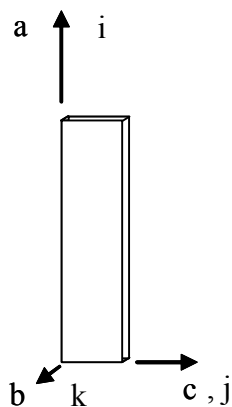
Figure S2. Crystal structure of (DT-TTF)[Cu(pdt)₂] (**5**). a) View of the dimerized DT-TTF molecules layer along the *a* axis, b) in a perpendicular view to the *a* axis of the dimerized chain, and c) a side view of the dimers enlarging the chain through S⋯S contacts (dotted lines) along *a*.



EPR studies on oriented single crystals at different temperatures

DT₄[Au(pds)₂]₃ (1)

Indexation: *a* (the shortest axis in cell) = *i* (the longest axis in the crystal); *b* = *k* (the shortest in crystal); and *c* (the longest in cell) = *j*



DT₄(Au(pds)₂)₃	300 K	200 K	135 K
g max (AHpp (G)) i; H//j	2.0092 (20.2)	2.0087 (35.6)	2.0082 (71)
g med (AHpp(G)) j; H//i	2.0052 (15.9)	2.0055 (23.2)	2.0060 (37.9)
g min (AHpp(G)) i; H//k	2.0006 (16.7)	2.0008 (25.7)	2.0014 (48)

DT₄[Au(bdt)₂]₃ (2)

Indexation: a (the shortest in cell) = i (the longest axis in the crystal); b = k (the shortest in crystal); and c (the longest in cell) = j

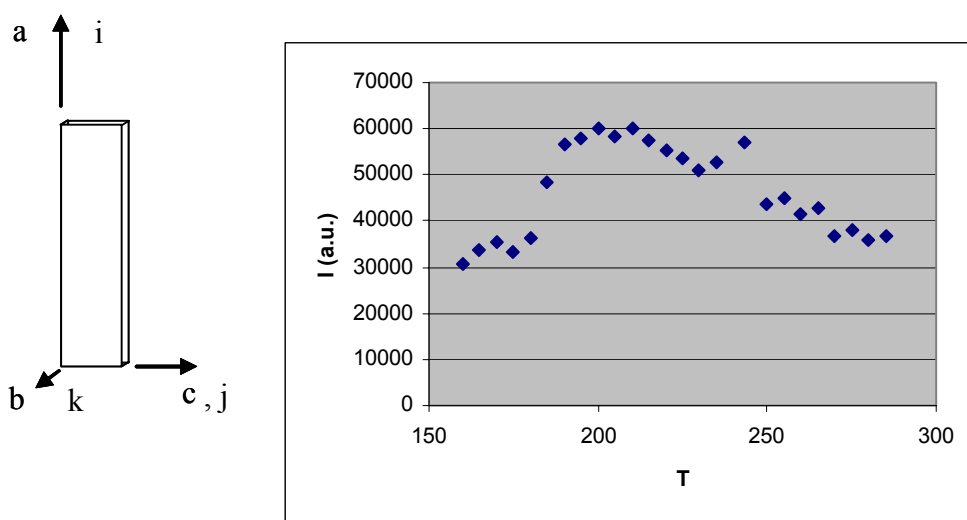


Figure S3. EPR intensity vs T plot for a single crystal of (DT-TTF)₄[Au(bdt)₂]₃ (2) oriented with the long macroscopic axis (i) perpendicular to the magnetic field H.

DT₄(Au(bdt)₂)₃	300 K
g max (AHpp (G)) i; H//j	2.0089 (16.2)
g med (AHpp(G)) j; H//i	2.0040 (20)
g min (AHpp(G)) i; H//k	1.9998 (14.4)

(DT-TTF)₄[Cu(pds)₂]₃ (3)

Indexation: *a* (the longest in cell) = *j*; *b* (the shortest in cell) = *i* (the longest in crystal); and *c* = *k* (the shortest in crystal)

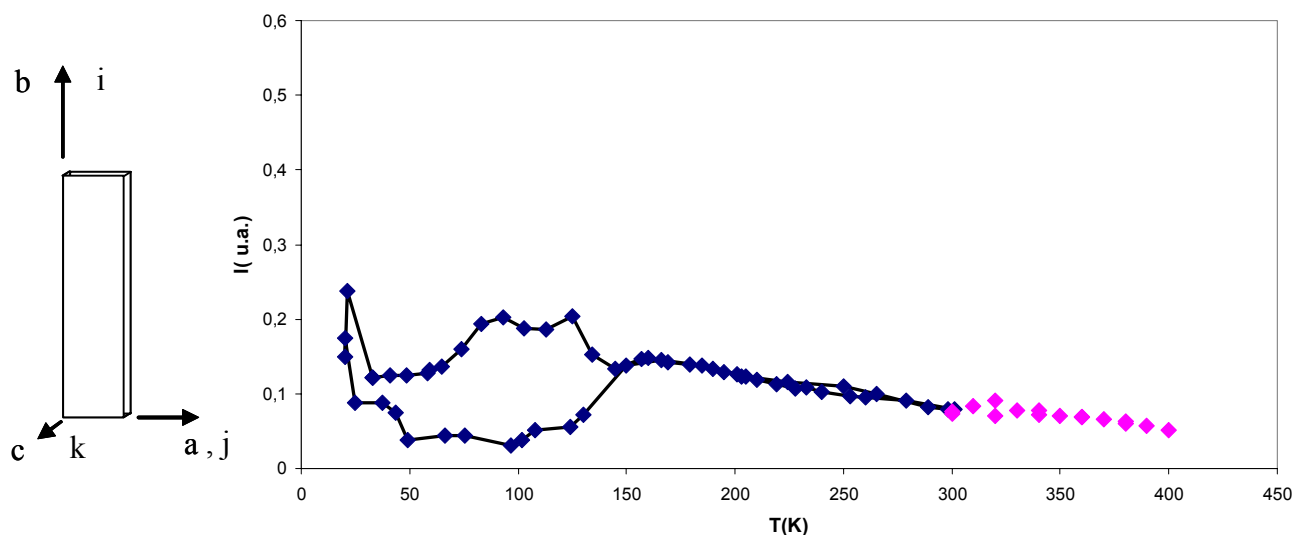
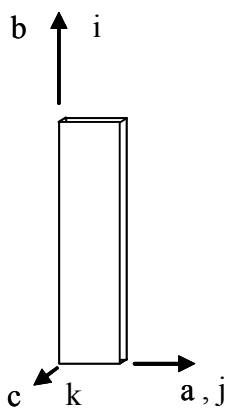


Figure S4. EPR intensity vs T plot for a single crystal of (DT-TTF)₄[Cu(pds)₂]₃ (3) oriented with the long macroscopic axis (*i*) perpendicular to the magnetic field *H*.

DT₄(Cu(pds)₂)₃	300 K	122 K
g max (AHpp (G)) i; H//j	2.0112 (15.3)	2.0101 (5.43)
g med (AHpp(G)) j; H//i	2.0068 (9.72)	2.0075 (3.6)
g min (AHpp(G)) i; H//k	2.00020 (10)	2.0020 (4.0)

DT₄[Cu(pdt)₂]₃ (4)

Indexation: a (the longest in cell) = j; b (the shortest in cell) = i (the longest in crystal); and c = k (the shortest in crystal)



DT₄(Cu(pdt)₂)₃	300 K	160 K
g max (AHpp (G)) i; H/j	2.0123 (1.52)	2.0121 (0.97)
g med (AHpp(G)) j; H/i	2.0061 (1.20)	2.0062 (0.69)
g min (AHpp(G)) i; H/k	2.00015 (1.17)	2.0015 (0.77)

¹ Mas-Torrent, M.; Hadley, P.; Bromley, S. T.; Ribas, X.; Tarrés, J.; Mas, M.; Molins, E.; Veciana, J.; Rovira, C. *J. Am. Chem. Soc.* **2004**, *126*, 8546-8563.

² (a) Kobayashi, H.; Kobayashi, A.; Sasaki, Y.; Saito, G.; Inokuchi, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 301. (b) Novoa, J. J.; Rovira, M. C.; Rovira, C.; Veciana, J.; Tarrés, J. *Adv. Mater.* **1995**, *7*, 233-237.

³ a) Rovira, C.; Veciana, J.; Ribera, E.; Tarres, J.; Canadell, E.; Rousseau, R.; Mas, M.; Molins, E.; Almeida, M.; Henriques, R. T.; Morgado, J.; Schoeffel, J.-P.; Pouget, J.-P. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2324 ; b) Rovira, C. *Chem. Eur. J.* **2000**, *6*, 1723-1729; c) Ribera, E.; Rovira, C.; Veciana, J.; Tarrés, J.; Canadell, E.; Rousseau, R.; Molins, E.; Mas, M.; Schoeffel, J.-P.; Pouget, J.-P.; Morgado, J.; Henriques, R. T.; Almeida, M. *Chem. Eur. J.* **1999**, *5*, 2025-2039; d) Ribas, X.; Mas-Torrent, M.; Pérez-Benítez, A.; Dias, J. C.; Alves, H.; Lopes, E. B.; Henriques, R. T.; Molins, E.; Santos, I. C.; Wurst, K.; Foury-Leylekian, P.; Almeida, M. Veciana, J.; Rovira, C., *Adv. Funct. Mater.*, in press.

⁴ Ribas, X.; Mas-Torrent, M.; Rovira, C.; Veciana, J.; Dias, J. C.; Alves, H.; Lopes, E. B.; Almeida, M.; Wurst, K. *Polyhedron* **2003**, *22*, 2415-2422.