Supporting Information:

Structural relations in (1:1) and (2:1) Cyanobenzene-Ethylenedithio-TTF radical salts; The role of C-N··· Interactions.

Gonçalo Lopes[a], Vasco Gama[a,b], Dulce Simão[c], Isabel Cordeiro Santos[a, b], Elsa B. Lopes[a, b], Laura C. J. Pereira[a, b], Manuel Almeida[a, b] and Sandra Rabaça[a,*]

[a] *C²TN, Centro de Ciências e Tecnologias Nucleares, Instituto Superior Técnico, Universidade de Lisboa, E.N. 10 ao km 139,7, 2695-066 Bobadela LRS, Portugal*
[b] *DECN, Departamento de Engenharia e Ciências Nucleares, Instituto Superior Técnico, Universidade de Lisboa, E.N. 10 ao km 139,7, 2695-066 Bobadela LRS, Portugal*
[c] *Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, P-1049-001 Lisboa, Portugal*

Table of Contents

Supplementary Tables

Table S1. ππ interactions in **1.**

Contacts	Symmetry operation (*)	Length(Å)	Length-∑VdW(Å)
C4…C7*	-x,-y,1-z	3.436	0.036
C5…C6*	-x,-y,1-z	3.394	-0.006
C6…C6*	-x,-y,1-z	3.406	0.006
C5…C11*	1-x,-y,1-z	3.470	0.070
C6…C9*	1-x,-y,1-z	3.414	0.014
C7…C7*	1-x,-y,1-z	3.447	0.047

Table S2. ππ interactions in **2.**

Contacts	Symmetry operation (*)	Length(Å)	Length-∑VdW(Å)
C6… C6*	1-x,1-y,1-z	3.222	-0.178
C6… C5*	1-x,1-y,1-z	3.420	0.020
C4… C7*	1-x,1-y,1-z	3.494	0.094
C4… C9*	1-x,1-y,1-z	3.469	0.069
C6… C9*	-x,1-y,1-z	3.423	0.023
C6… C11*	-x,1-y,1-z	3.418	0.018
C5… C11*	-x,1-y,1-z	3.464	0.064
C7… C7*	-x,1-y,1-z	3.337	-0.063

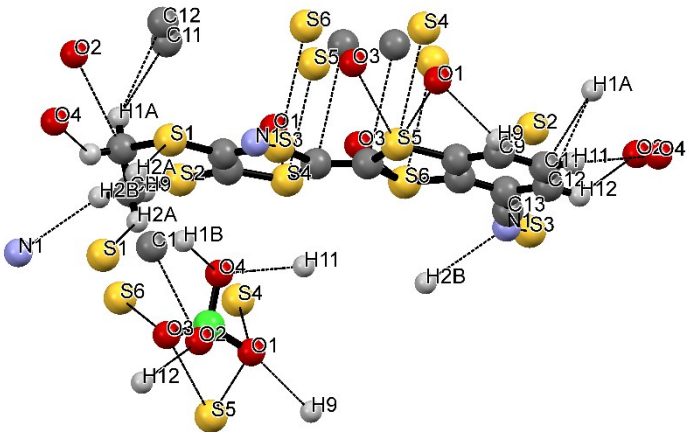


Table S3. Short contact list of compound [*4*-CNB-EDT-TTF]ClO_4 (**1**)

	Short Contacts	Symmetry operation (*)	Length(Å)	Length-∑VdW(Å)
Intra-dimer	S3···S6*	-x,-y,1-z	3.433	-0.167
Intra-dimer	S4···S5*	-x,-y,1-z	3.323	-0.277
Intra-dimer	H1A···C11*	-x,-y,1-z	2.867	-0.033
Intra-dimer	H1A···C12*	-x,-y,1-z	2.862	-0.038
Intra-dimer	C5···C6*	-x,-y,1-z	3.394	-0.006
Inter-dimer	S2···H9*	-1+x,1+y,z	2.990	-0.010
Inter-dimer	S1···H2A*	-x,1-y,-z	2.988	-0.012
Inter-dimer	C13-N1···S3*	x,y,1+z	3.291	-0.059
Inter-dimer	C13-N1···H2B-C2*	-x,1-y,1-z	2.710	-0.040
Dimer-anion	O2···H12*	x,1+y,-1+z	2.630	-0.090
Dimer-anion	O1···S5*	x,1+y,z	2.987	-0.333
Dimer-anion	O1···H9*	x,1+y,z	2.527	-0.193
Dimer-anion	O3···S5*	x,1+y,z	3.112	-0.208
Dimer-anion	O2···C1*	-x,1-y,-z	3.182	-0.038
Dimer-anion	O4···H1B*	-x,1-y,-z	2.621	-0.099
Dimer-anion	O1···S4*	-x,1-y,1-z	3.308	-0.012
Dimer-anion	O3···S6*	-x,1-y,1-z	3.299	-0.021
Dimer-anion	O4···H11*	1-x,-y,1-z	2.442	-0.278

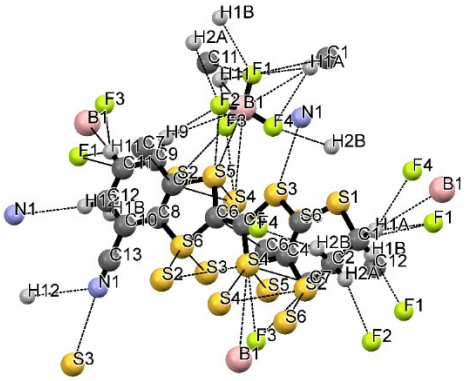


Table S4. Short contact list of compound [*4*-CNB-EDT-TTF]BF_4 (**2**)

	Short Contacts	Symmetry operation (*)	Length(Å)	Length-∑VdW(Å)
Intra-dimer	S6···S3*	3.520	-0.080	1-x,1-y,1-z
Intra-dimer	S4···S5*	3.373	-0.227	1-x,1-y,1-z
Intra-dimer	S4···C7*	3.433	-0.067	1-x,1-y,1-z
Intra-dimer	C6···C6*	3.222	-0.178	1-x,1-y,1-z
Intra-dimer	C12···H1B*	2.894	-0.006	1-x,1-y,1-z
Inter-dimer	C7···C7*	3.337	-0.063	-x,1-y,1-z
Inter-dimer	S6···S2*	3.585	-0.015	1-x,2-y,1-z
Inter-dimer	S4···S4*	3.590	-0.010	1-x,2-y,1-z
Inter-dimer	S4···S2*	3.549	-0.051	1-x,2-y,1-z
Inter-dimer	S3···N1*-C13*	3.288	-0.062	x,y,-1+z
Inter-dimer	C13-N1···H12*-C12*	2.709	-0.041	-x,1-y,2-z
Dimer-anion	S5···F2*	2.938	-0.332	x,y,z
Dimer-anion	S5···B1*	3.573	-0.227	x,y,z
Dimer-anion	H9···F2*	2.447	-0.223	x,y,z
Dimer-anion	H9···B1*	3.169	-0.031	x,y,z
Dimer-anion	H2B···F4*	2.538	-0.132	x,1+y,z
Dimer-anion	H2A···F2*	2.604	-0.066	1+x,1+y,z
Dimer-anion	H1B···F1*	2.474	-0.196	1+x,1+y,z
Dimer-anion	C11···F1*	3.159	-0.011	-x,-y,1-z
Dimer-anion	H11···F1*	2.436	-0.234	-x,-y,1-z
Dimer-anion	H11···F3*	2.353	-0.317	-x,-y,1-z
Dimer-anion	H11···B1*	2.904	-0.296	-x,-y,1-z
Dimer-anion	C1···F1*	3.131	-0.039	1-x,1-y,-z
Dimer-anion	H1A···F1*	2.266	-0.404	1-x,1-y,-z
Dimer-anion	H1A···F4*	2.666	-0.004	1-x,1-y,-z
Dimer-anion	H1A···B1*	2.962	-0.238	1-x,1-y,-z
Dimer-anion	S4···F3*	2.888	-0.382	1-x,1-y,1-z
Dimer-anion	S4···B1*	3.704	-0.096	1-x,1-y,1-z
Dimer-anion	S2···F3*	3.186	-0.084	1-x,1-y,1-z

Table S5. ππ interactions in **3.**

Contacts	Symmetry operation (*)	Length(Å)	Length-∑VdW(Å)
C15… C5*	x,y,z	3.589	0.189
C17… C3*	x,y,z	3.576	0.176
C14… C11*	1-x,1-y,-z	3.522	0.122
C14… C12*	1-x,1-y,-z	3.539	0.139
C16… C11*	1-x,1-y,-z	3.376	-0.024
C16… C11*	1-x,1-y,-z	3.376	-0.024
C5… C5*	1-x,1-y,-z	3.332	-0.068

Table S6. ππ interactions in **4.**

Contacts	Symmetry operation (*)	Length(Å)	Length-∑VdW(Å)
C17… C3*	x,y,z	3.580	0.180
C14… C11*	1-x,1-y,-z	3.531	0.131
C14… C12*	1-x,1-y,-z	3.595	0.195
C16… C11*	1-x,1-y,-z	3.413	0.013
C5… C5*	1-x,1-y,-z	3.393	-0.007
C5…C6*	1-x,1-y,-z	3.561	0.161

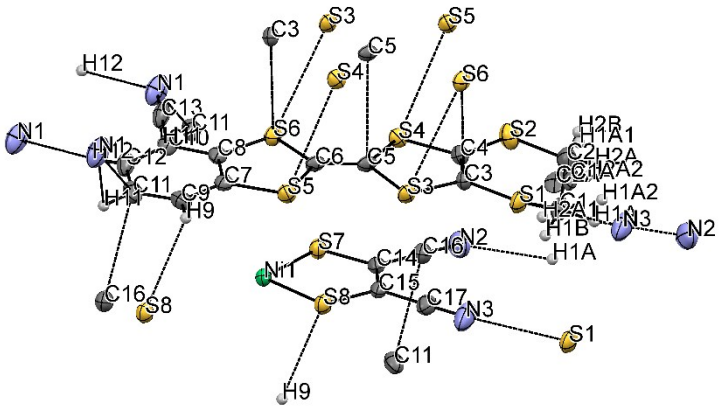


Table S7. Short contact list of compound [*4*-CNB-EDT-TTF]$_2$[Ni(mnt)$_2$] (**3**)

	Short Contacts	**Symmetry operation (*)**	**Length(Å)**	**Length-∑VdW(Å)**
Intra-dimer DD	S3···S6*	1-x,1-y,-z	3.591	-0.009
Intra-dimer DD	S4···S5*	1-x,1-y,-z	3.587	-0.013
Intra-dimerDD	S6···C3*	1-x,1-y,-z	3.497	-0.003
Intra-dimer DD	C5···C5*	1-x,1-y,-z	3.332	-0.068
Intra-stack DA	C16···C11*	1-x,-y,-z	3.376	-0.024
Lat Inter-stack DA	S8···H9*	-x,-y,-z	2.860	-0.140
Lat Inter-stack DD	C11···N1*-C13*	-1+x,y,z	3.104	-0.146
Lat Inter-stack DD	H11···N1	-1+x,y,z	2.708	-0.042
Inter-stack DA	C17-N3···S1*	1-x,1-y,1-z	3.162	-0.188
Inter-stack AD	C16-N2···H1A*-C1*	2-x,1-y,1-z	2.507	-0.243
Inter-stack DD	C13-N1···H12*-C12*	1-x,-y,-1-z	2.446	-0.304

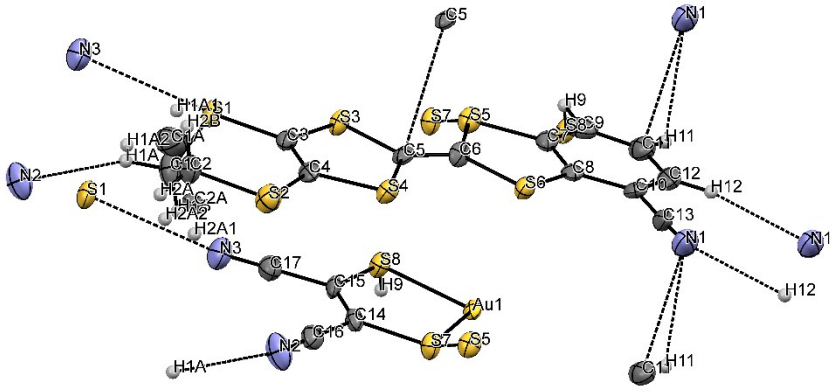


Table S8. Short contact list of compound [*4*-CNB-EDT-TTF]$_2$[Au(mnt)$_2$] (**4**)

	Short Contacts	**Symmetry operation (*)**	**Length(Å)**	**Length-∑VdW(Å)**
Intra-dimer DD	C5···C5*	1-x,1-y,-z	3.393	-0.007
Lat Inter-stack DA	S7···S5*	1+x,y,z	3.579	-0.021
Lat Inter-stack DA	S8···H9*	-x,-y,-z	2.903	-0.097
Lat Inter-stack DD	C11···N1*-C13*	-1+x,y,z	3.095	-0.155
Lat Inter-stack DD	H11···N1*-C13*	-1+x,y,z	2.705	-0.045
Inter-stack DA	C17-N3···S1*	1-x,1-y,1-z	3.160	-0.190
Inter-stack DA	C16-N2···H1A*-C1*	2-x,1-y,1-z	2.519	-0.231
Inter-stack DD	C13-N1···H12*-C12*	1-x,-y,-1-z	2.445	-0.305

Supplementary Figures

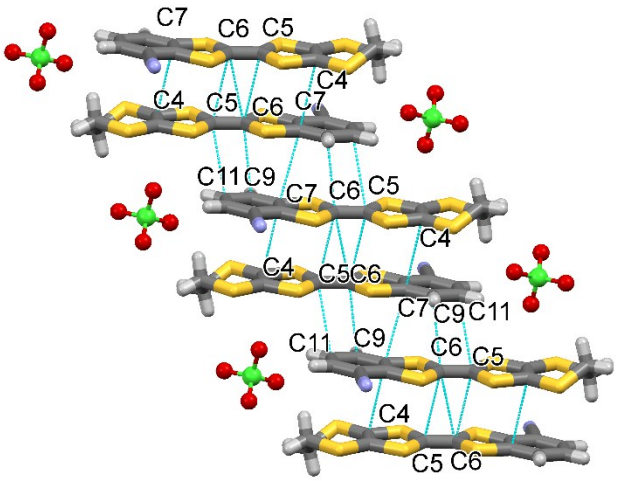


Figure S1. Crystal structure details of the ππ nteractions in the salt **1**.

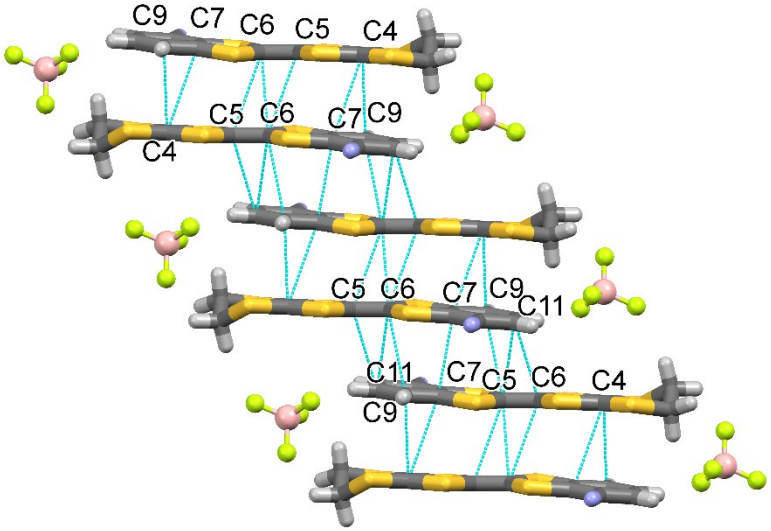


Figure S2. Crystal structure details of the ππ interactions in the salt **2**.

a) b)

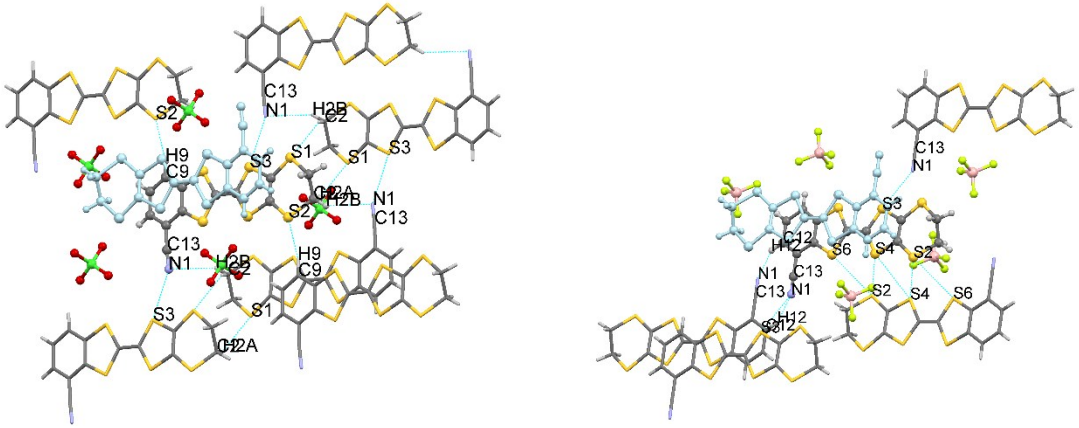
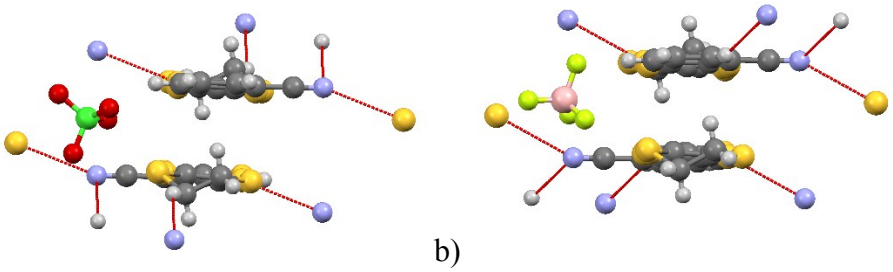


Figure S3. Arrangement of the interstack donor-donor contacts in reference to one donor in **1** a) and **2** b).



a) b)

Figure S4. CN··· interaction details on: a) [*4*-CNB-EDT-TTF]ClO_4 (**1**); b) [*4*-CNB-EDT-TTF]BF_4 (**2**) donor dimers.

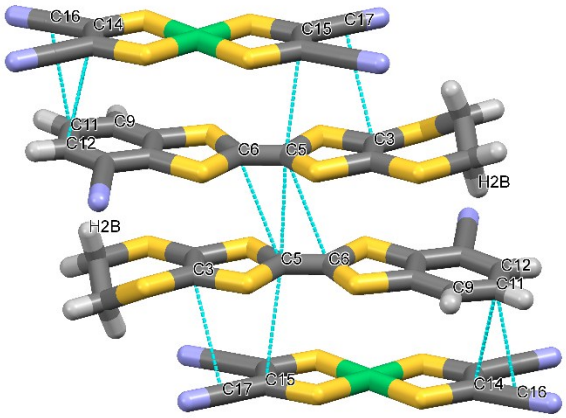


Figure S5. Crystal structure details of the ππ interactions in salt **3**.

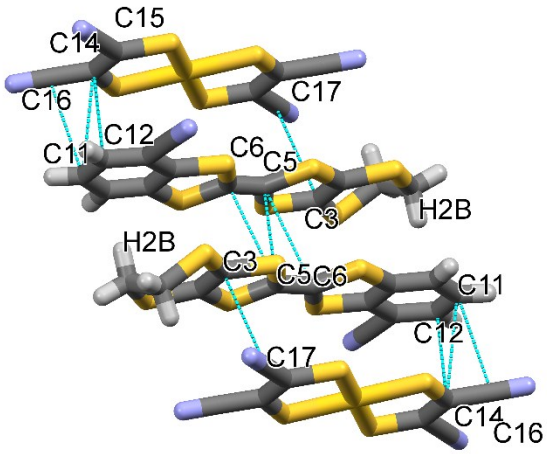


Figure S6. Crystal structure details of the ππ ınteractions in salt **4**.

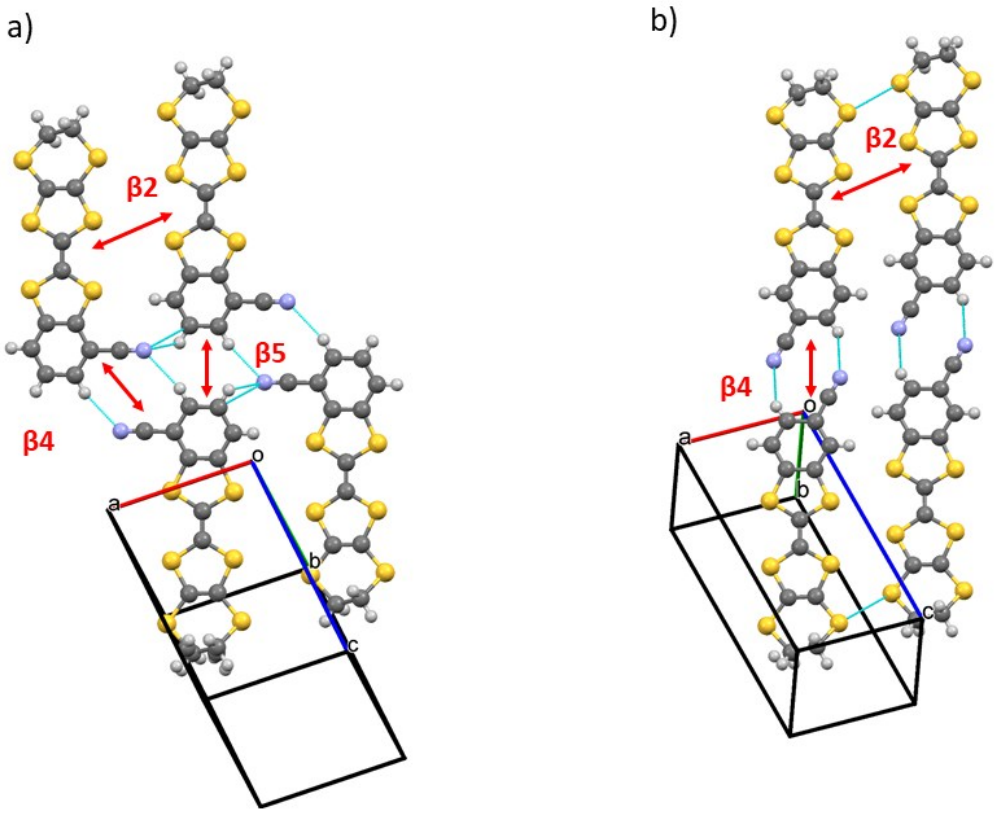


Figure S7. Partial view of the **(a)** *4*-CNB-EDT-TTF and **(b)** *5*-CNB-EDT-TTF donors arrangement in salts **3** and **4** and in (*5*-CNB-EDT-TTF)$_2$[M(mnt)$_2$] salts. The arrows denote the different interdonor interactions

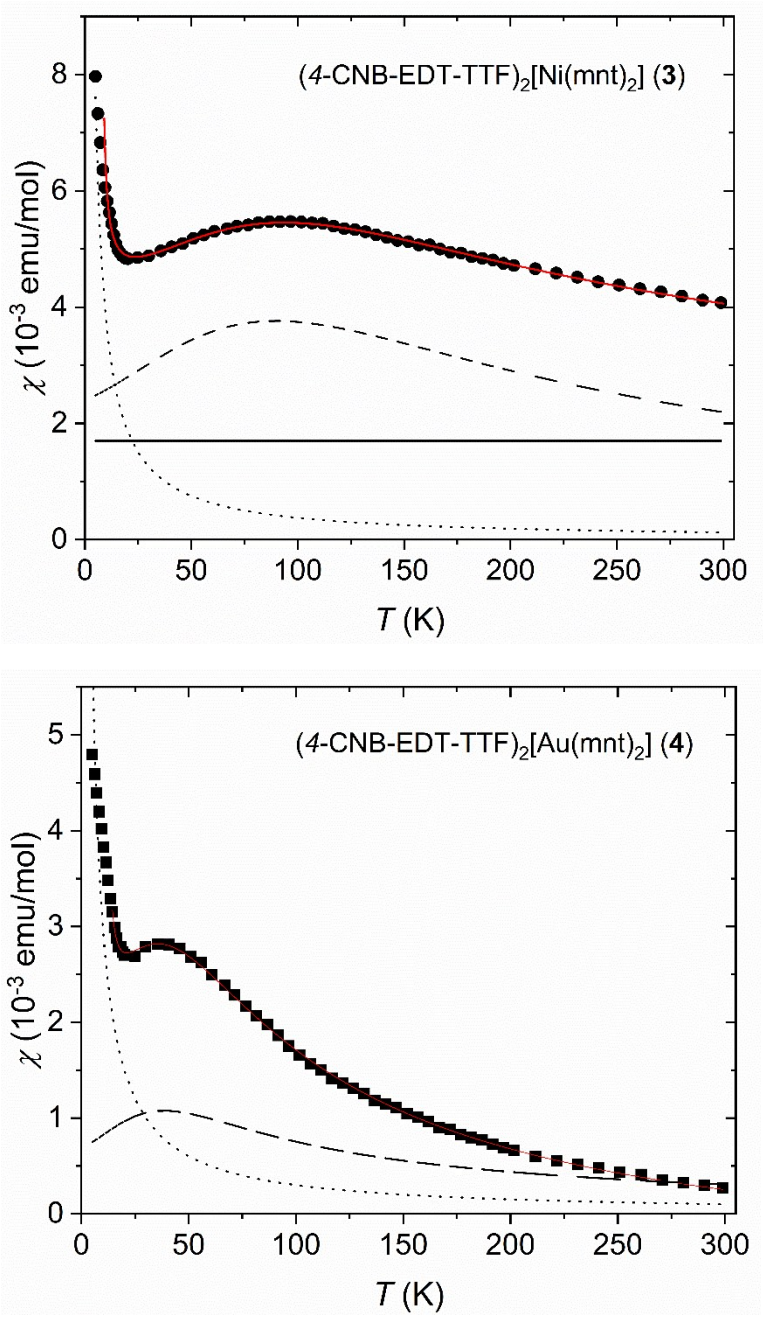


Figure S8. Temperature dependence of the paramagnetic susceptibility, χ_p, of compounds **3** (up) and **4** (bottom) with the correspondent fits to equation **1** (thick solid line) as explained in the main text. The corresponding contributions; TIP (thin solid line), Curie (dotted line), and dimer (dashed line) contributions are also represented.

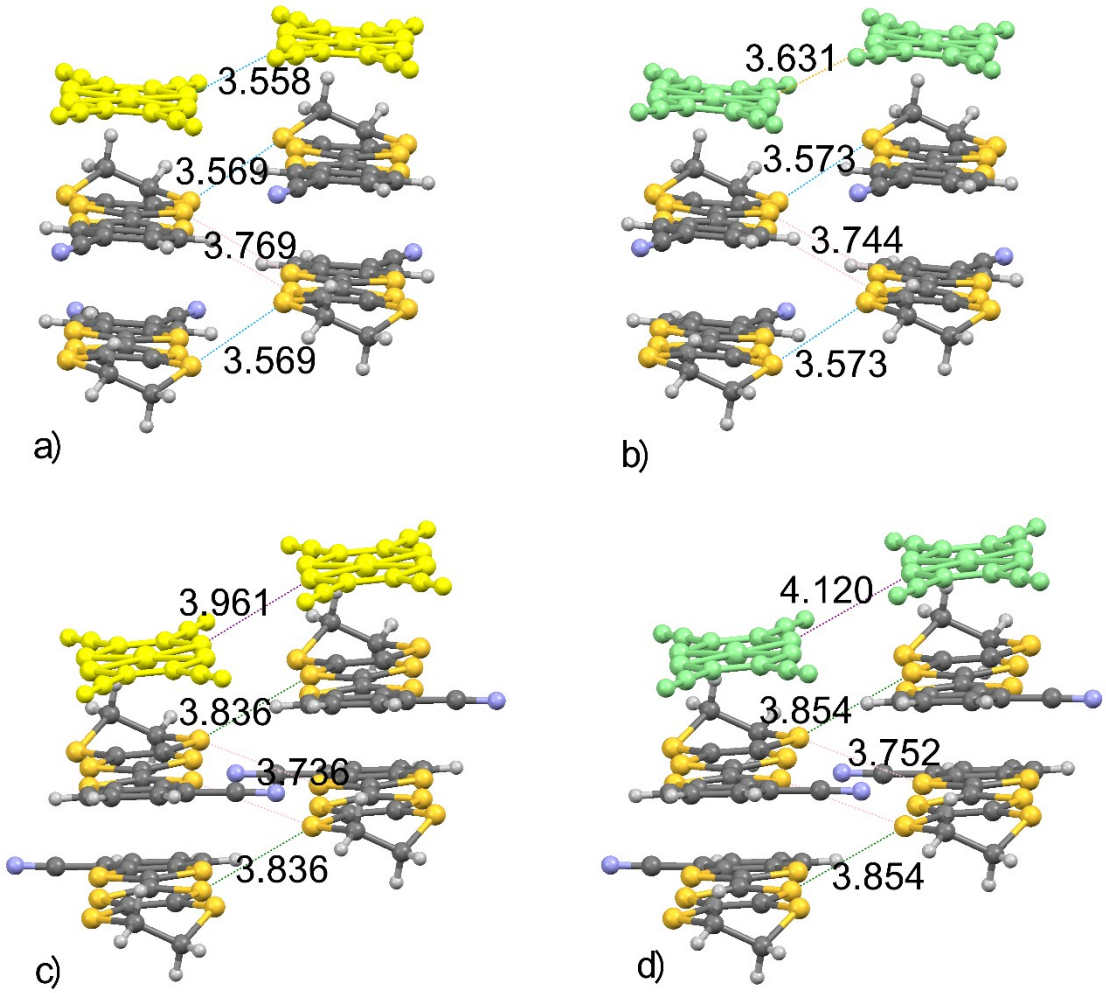


Figure S9. Detail of the interstack arrangement of the donors and anions, illustrating the shortest DD and AA S···S separations (dashed lines) for (*5*-CNB-EDT-TTF)$_2$[M(mnt)$_2$] (M=Au (a) and Ni (b)), **3** and **4** (c and d). The DD and AA contacts give rise to the chains of donor dimers that propagate along *a*. It is possible to observe that the DD and AA separations are considerably larger in **3** and **4** than in the corresponding *5*-CNB-EDT-TTF analogues, which is quite in good agreement with the significantly weaker magnetic coupling observed for **3** and **4**.