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Supplementary Material for

Cyano Benzene Functionalized Ni and Cu Bisdithiolene Complexes

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Table SM1: Cyclic voltammetry data of [M(L)2] (M= Ni, Cu); L=3-cbdt and 4-cbdt in acetonitrile (ref. Ag/AgNO3)

	$[M(L)_2]^0/[M(L]_2]^-$ (V)	$[M(L)_2]^-/[M(L]_2]^{2-}$ (V)	Solvent	Ref
$[Ni(4\text{-}cbdt)_2]$	+0.20	-0.51	CH_3CN	1
$[Ni(3\text{-}cbdt)_2]$	+0.281	-0.31	CH_3CN	This work
$[Cu(4\text{-}cbdt)_2]$	+0.69	-0.64	CH_3CN	1
$[Cu(3\text{-}cbdt)_2]$	+0.71	-0.61	CH_3CN	This work

1. Cerdeira, Ana C., et al. "Synthesis, structure and physical properties of transition metal bis 4-cyanobenzene-1, 2-dithiolate complexes [M (cbdt) 2] z−(M= Zn, Co, Cu, Au, Ni, Pd, z= 0, 1, 2)." Polyhedron 44.1 (2012): 228-237.

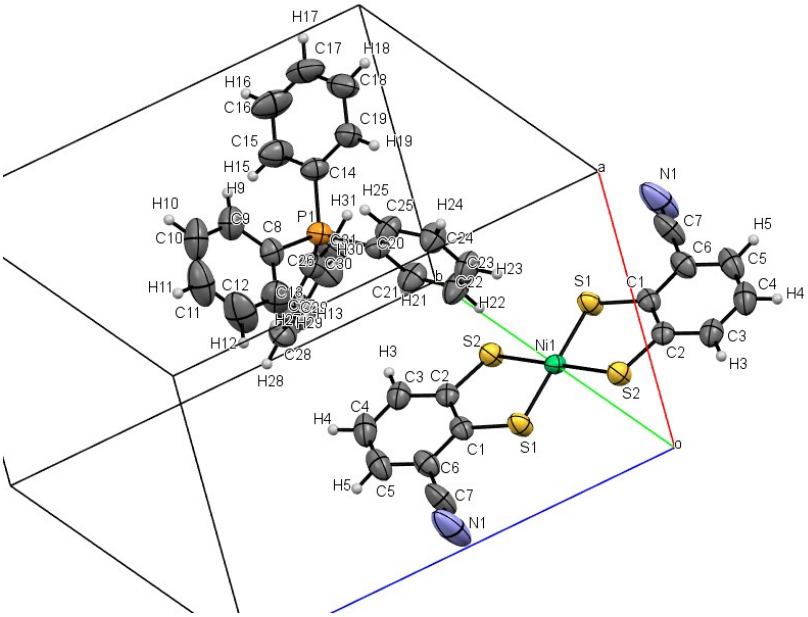


Figure SM1. ORTEP diagram of **α1**.

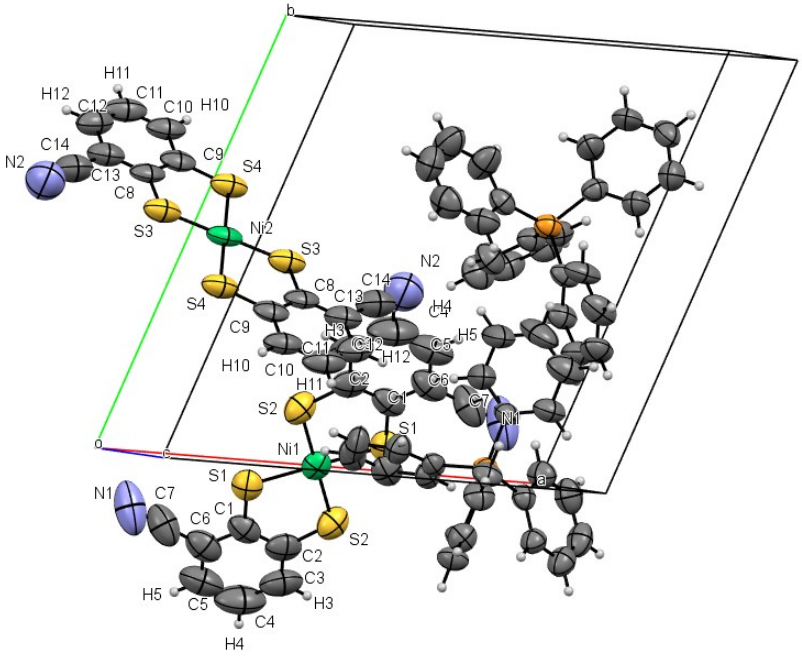


Figure SM2. ORTEP diagram of **β1**. For clarity, the TPP numbering scheme was omitted.

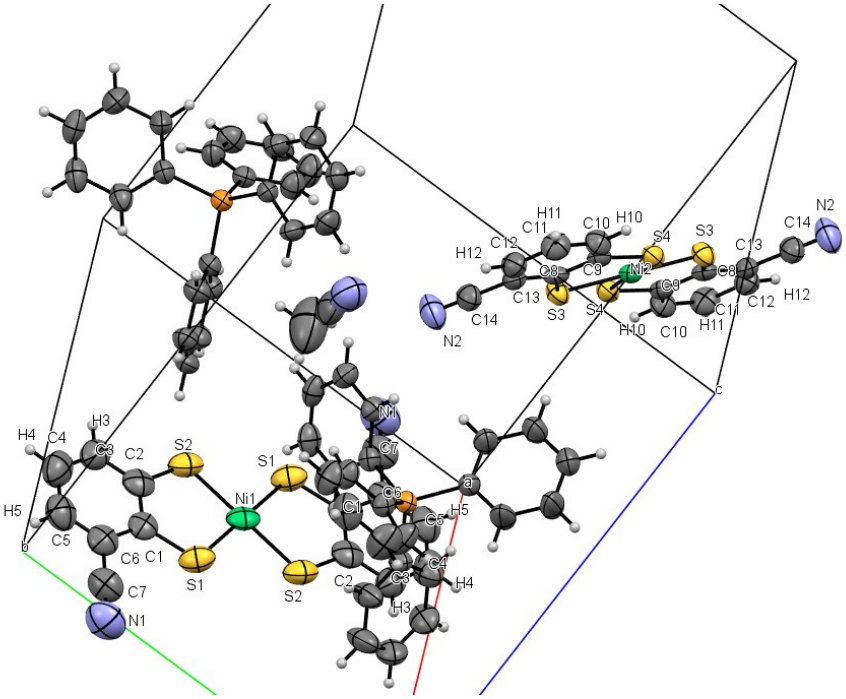


Figure SM3. ORTEP diagram of **1CH$_3$CN**. For clarity, the TPP numbering scheme was omitted.

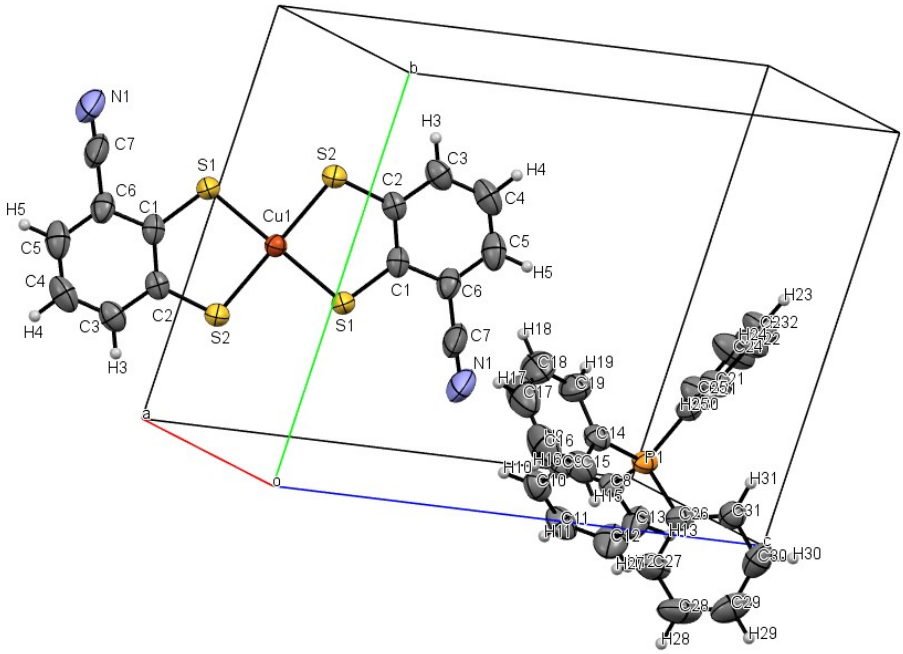


Figure SM4. ORTEP diagram of **α3**.

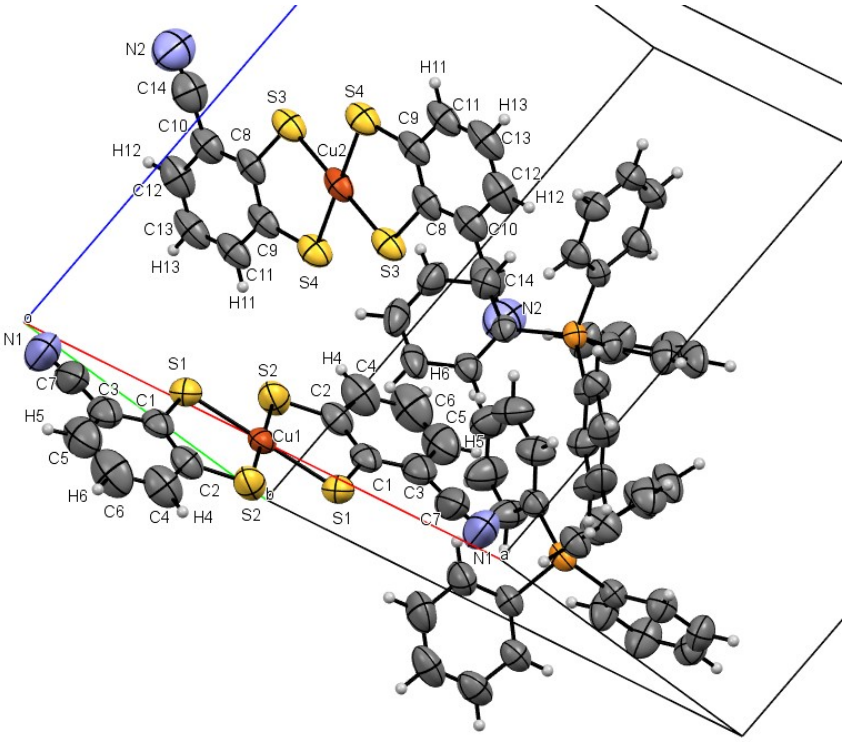


Figure SM5. ORTEP diagram of **β3**. For clarity, the TPP numbering scheme was omitted.

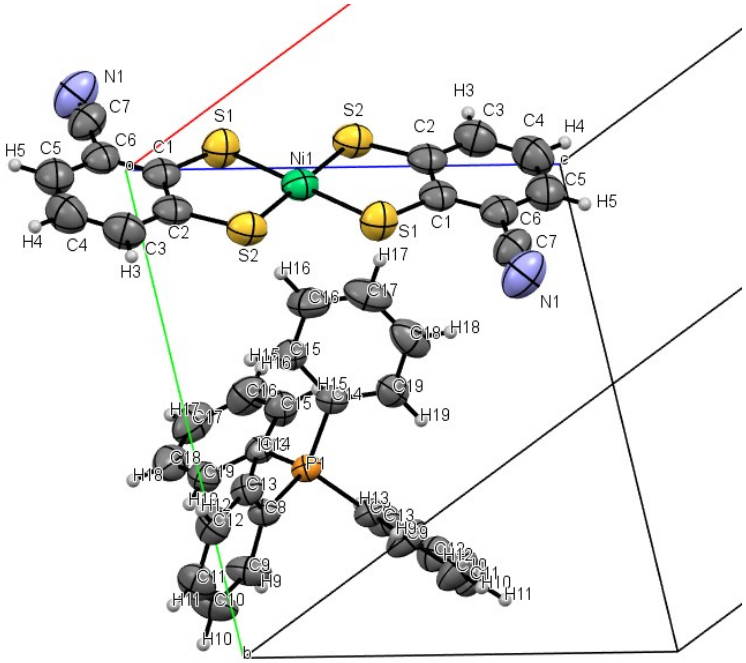


Figure SM6. ORTEP diagram of **α2**.

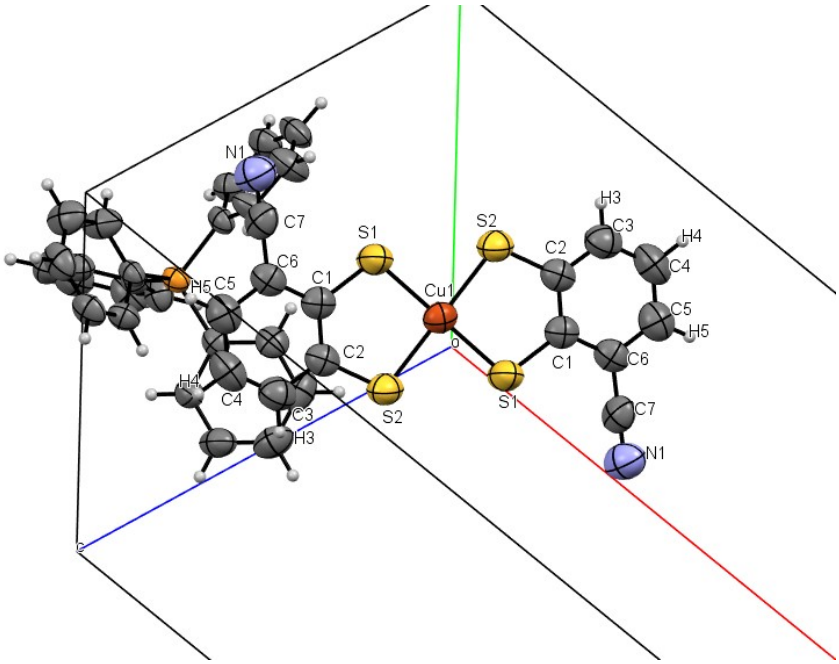


Figure SM7. ORTEP diagram of **α4**. For clarity, the TPP numbering scheme was omitted.

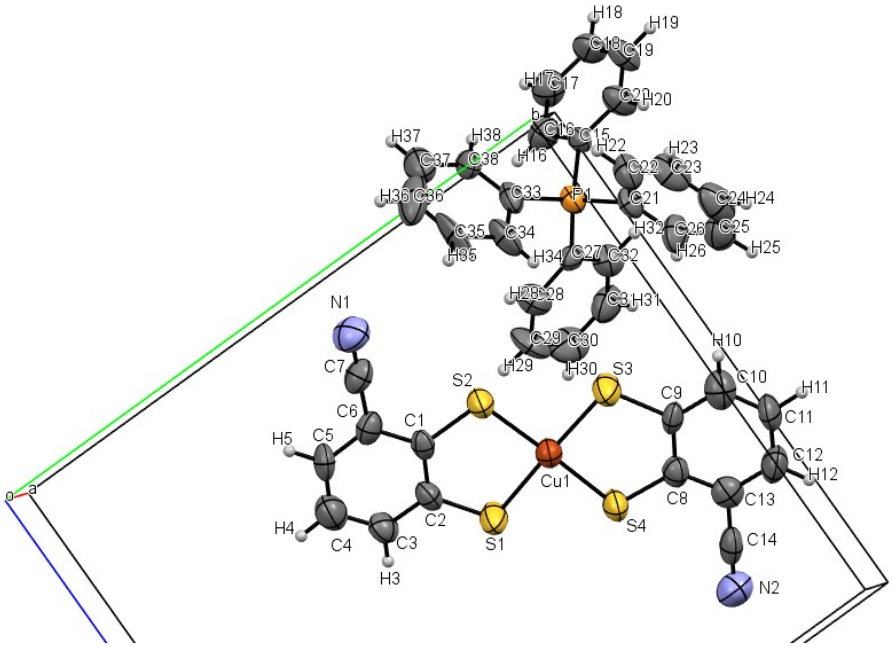
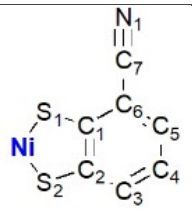


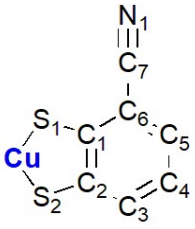
Figure SM8. ORTEP diagram of β4.

Table SM2: Intermolecular bond lengths (Å) in dianionic and monanionic dithiolene complexes $[Ni(3\text{-cbdt})_2]^{-n}$, (n=1, 2).)

	**dianion**			**monoanion**
	α-1	**β-1**	**1.CH3CN**	**2-α**
Ni-S1	2.1664	2.176	2.176	2.1552
		2.140	2.140	
Ni-S2	2.1793	2.168	2.168	2.1407
		2.189	2.189	
S1-C1	1.733(2)	1.737(7)	1.737(7)	1.726(4)
		1.737(6)	1.737(6)	
S2-C2	1.744(2)	1.72(1)	1.72(1)	1.742(3)
		1.718(7)	1.718(7)	
C1-C2	1.406(3)	1.41(1)	1.41(1)	1.395(4)
		1.397(9)	1.397(9)	
C2-C3	1.397(3)	1.39(1)	1.39(1)	1.397(5)

		1.408(8)	1.408(8)	
C3-C4	1.382(4)	1.41(2)	1.41(2)	1.368(5)
		1.36(1)	1.36(1)	
C4-C5	1.369(4)	1.37(2)	1.37(2)	1.384(6)
		1.36(1)	1.36(1)	
C6-C5	1.400(4)	1.39(1)	1.39(1)	1.366(5)
		1.41(1)	1.41(1)	
C1-C6	1.414(3)	1.41(2)	1.41(2)	1.423(4)
		1.38(1)	1.38(1)	
C6-C7	1.429(4)	1.42(2)	1.42(2)	1.436(5)
		1.40(1)	1.40(1)	
C7-N1	1.142(4)	1.15(1)	1.15(1)	1.136(5)
		1.15(1)	1.15(1)	

Table SM2: Intermolecular bond lengths (Å) in dianionic and monanionic dithiolene complexes $[Cu(3\text{-cbdt})_2]^{-n}$, (n=1, 2).)



	dianion		monoanion	
	α-3	**β-3**	**α-4**	**β-4**
Cu-S1	2.2536	2.287	2.172	2.183(4)
		2.262		2.171(4)
Cu-S2	2.2769	2.2539	2.170	2.163(4)
		2.2814		2.183(4)
S1-C1	1.726(3)	1.746(3)	1.740(6)	1.75(1)
		1.751(3)		1.73(1)
S2-C2	1.739(3)	1.734(4)	1.753(6)	1.72(1)
		1.740(4)		1.78(1)
C1-C2	1.409(4)	1.405(5)	1.373(7)	1.39(2)
		1.407(5)		1.42(2)

C2-C3	1.394(5)	1.404(5)	1.38(1)	1.36(2)
		1.400(4)		1.38(2)
C3-C4	1.376(5)	1.377(9)	1.38(1)	1.38(2)
		1.370(6)		1.36(2)
C4-C5	1.365(6)	1.367(8)	1.379(9)	1.36(2)
		1.369(6)		1.38(2)
C6-C5	1.408(6)	1.403(6)	1.38(1)	1.38(2)
		1.403(5)		1.36(2)
C1-C6	1.409(4)	1.411(7)	1.410(8)	1.41(2)
		1.397(6)		1.38(2)
C6-C7	1.434(5)	1.437(8)	1.424(8)	1.45(2)
		1.430(6)		1.43(2)
C7-N1	1.140(6)	1.150(8)	1.131(8)	1.14(2)
		1.146(6)		

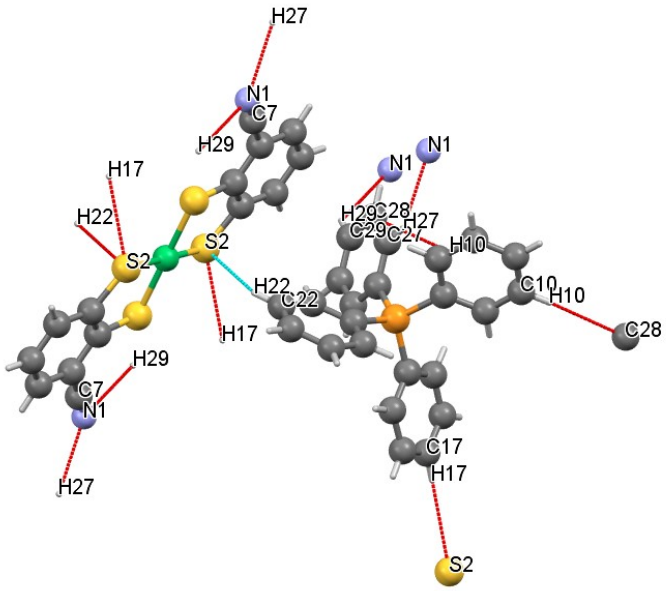


Table SM3: Short contacts list of compound **α1**

	Short Contacts	**Symmetry operation (*)**	**Length (Å)**	**Length-∑VdW (Å)**	
anion-anion	C5…C5	-x,1-y,11-z	3.446	0.046	π…π*1
	C5-H5…H5	-x,1-y,-z	2.943	0.043	C-H…π*1
cation-cation	C10-H10…C27	1-x, 2-y,1-z	2.994	0.094	C-H…π
	C10-H10…C28	1-x, 2-y,1-z	2.820	-0.080	C-H…π
anion-cation	S2…H17	1-x,2-y,-z	2.933	-0.067	
	S2…H22	x,y,z	2.965	-0.035	
	C25-H25…C4	1+x,y,z	2.975	0.075	C-H…π
	C25-H25…C3	1+x,y,z	2.910	0.010	C-H…π
	C25-H25…C2	1+x,y,z	2.907	0.007	C-H…π
	C27-H27…N1-C7	-x,1-y,1-z	2.532	-0.218	C-H…N≡C
	C29-H29…N1-C7	x,1+y,x	2.729	-0.021	C-H…N≡C

*1 offset pi/pi stacking

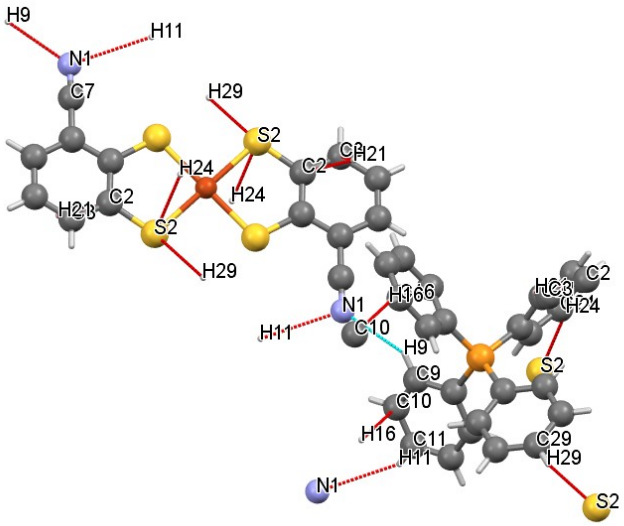


Table SM4: Short contacts list of compound **α-3**

	Short Contacts	Symmetry operation (*)	Length (Å)	Length-∑VdW (Å)	
anion-anion	C5…C5	1-x,1-y,1-z	3.440	0.040	π…π*1
	C5…H5	1-x,1-y,1-z	2.929	0.029	C-H…π*1
cation-cation	C16-H16…C9	-x,-y,1-z	2.992	0.092	C-H…π
	C16-H16…C10	-x,-y,1-z	2.832	-0.068	C-H…π
anion-cation	S2…H29	1+x,1+y,-1+z	2.932	-0.068	
	S2…H24	1-x,1-y,1-z	2.980	-0.020	
	C21-H21…C2	-x,1-y,1-z	2.899	-0.001	C-H…π
	C21-H21…C3	-x,1-y,1-z	2.896	-0.004	C-H…π
	C9-H9…N1-C7	x,y,z	2.529	-0.221	C-H…N≡C
	C11-H11…N1-C7	1-x,-y,1-z	2.747	-0.003	C-H…N≡C

*1 offset pi/pi stacking

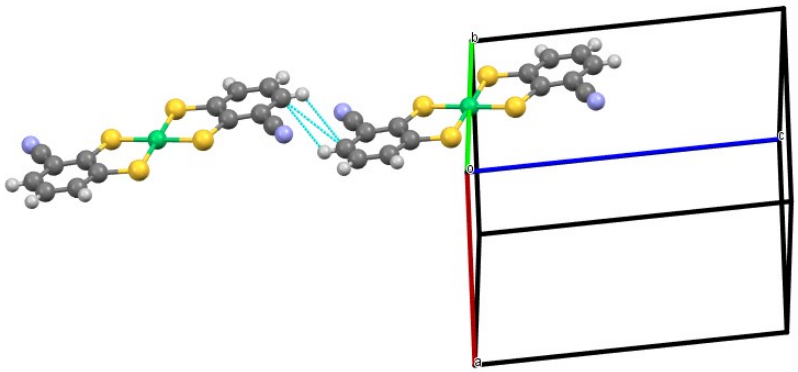


Figure SM9. Detail of the C5···C5 and C5···H5 interactions in compound **α-1**

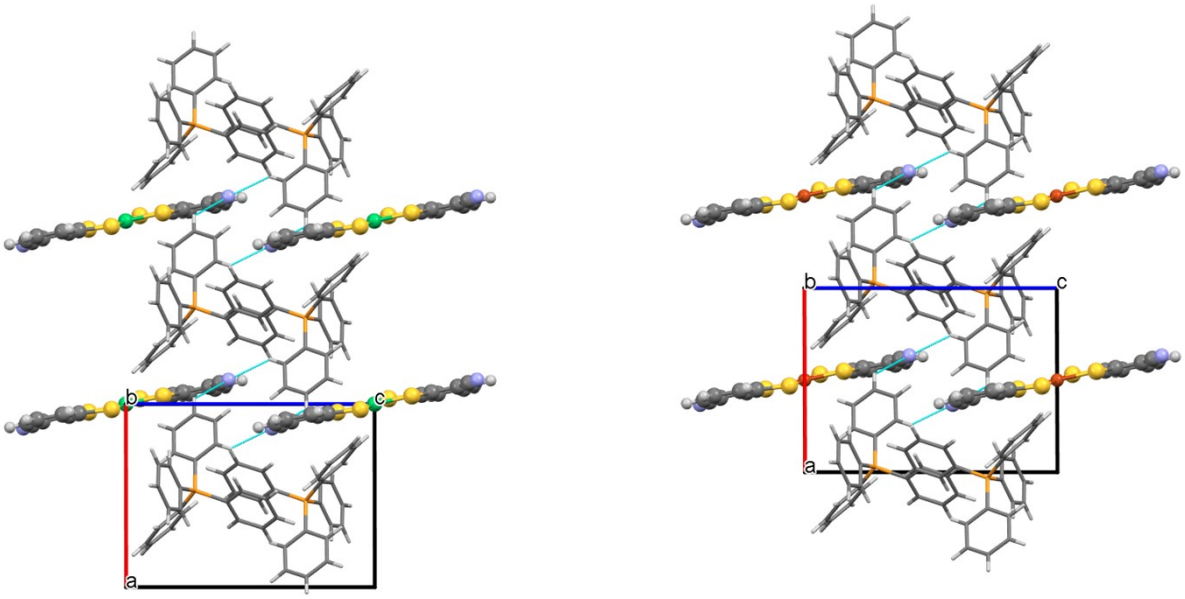


Figure SM10. Structural detail of the $R^2_4(12)$ synthons mediated by the C-H···N≡C short contacts, in **α-1** (left) and **α-3** (right).

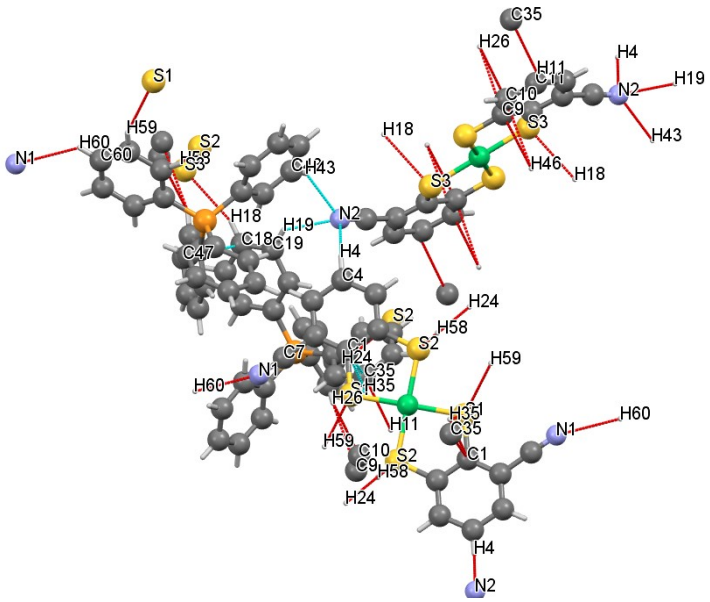


Table SM5: Short contact list of compound **β1**

	Short Contacts	Symmetry operation (*)	Length (Å)	Length-∑VdW (Å)	
anion-anion	C4-H4…N2≡C14	x,y,z	2.626	-0.124	C-H…N≡C
cation-cation	C18…C47	x,y,z	3.308	-0.092	π…π*1/2
anion-cation	S1…H35	x,y,z	2.912	-0.088	
	S1…H59	x,-1+y,z	2.874	-0.126	
	S2…H24	1-x,-y,1-z	2.993	-0.007	
	S2…H58	1-x,1-y,-z	2.749	-0.251	
	S3…H18	1-x,1-y,1-z	2.681	-0.319	
	C60-H60…N1-C7	2-x,1-y,-z	2.667	-0.083	C-H…N≡C
	C19-H19…N2-C14	x,y,z	2.539	-0.211	C-H…N≡C
	C43-H43…N2-C14	x,y,z	2.588	-0.162	C-H…N≡C
	C11-H11…C35	1-x,-y,1-z	2.836	-0.064	C-H…π*1
	C26-H26…C9	1-x,-y,1-z	2.679	-0.221	C-H…π*2
	C46-H46…C9	1-x,-y,1-z	2.730	-0.170	C-H…π*2
	C26-H26…C10	1-x,-y,1-z	2.634	-0.233	C-H…π*2
	C46-H46…C10	1-x,1-y,1-z	2.772	-0.128	C-H…π*2
	C1…C35	x,y,z	2.830	-0.070	π…π*1
	C35-H35…C1	x,y,z	2.836	-0.064	C-H…π*1
	C11-H11…C35	1-x,-y,1-z	2.836	-0.064	C-H…π*2

*1 offset pi/pi stacking

*2 aromatic CH/pi hydrogen bonds; edge-to-face; T-shape aromatic interaction

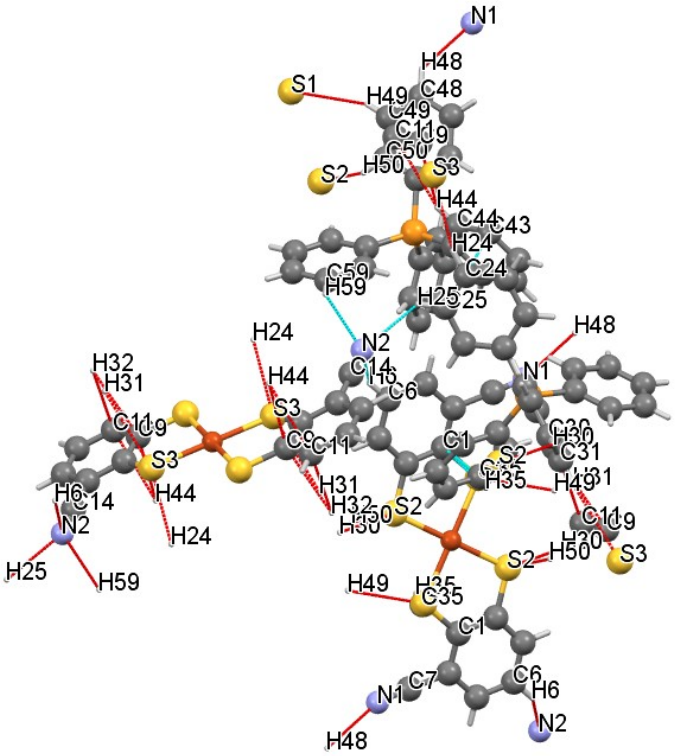


Table SM6: Short contacts list of compound **β-3**

	Short Contacts	Symmetry operation (*)	Length (Å)	Length-∑VdW (Å)	
anion-anion	C6-H6…N2-C14	x,y,z	2.709	-0.041	C-H…N≡C
cation- cation	C24…C43	x,y,z	3.330	-0.070	π…π
anion-cation	S1…H35	x,y,z	2.949	-0.051	
	S1…H49	1-x,-y,1-z	2.970	-0.030	
	S2…H30	x,-1+y,z	2.904	-0.096	
	S2…H50	1-x,1-y,-z	2.782	-0.218	
	S3…H31	1-x,-y,1-z	2.987	-0.013	
	S3…H24	1-x,1-y,1-z	2.675	-0.325	
	C48-H48…N1-C7	2-x,1-y,-z	2.713	-0.037	C-H…N≡C
	C25-H25…N2-C14	x,y,z	2.556	-0.194	C-H…N≡C
	C59-H59…N2-C14	x,y,z	2.599	-0.151	C-H…N≡C
	C35-H35…C1	x,y,z	2.826	-0.074	C-H…π
	C32-H32…C9	1-x,-y,1-z	2.689	-0.211	C-H…π
	C32-H32…C11	1-x,-y,1-z	2.644	-0.256	C-H…π
	C44-H44…C9	1-x,1-y,1-z	2.742	-0.158	C-H…π
	C44-H44…C11	1-x,1-y,1-z	2.772	-0.128	C-H…π
	C1…C35	x,y,z	3.270	-0.130	π…π

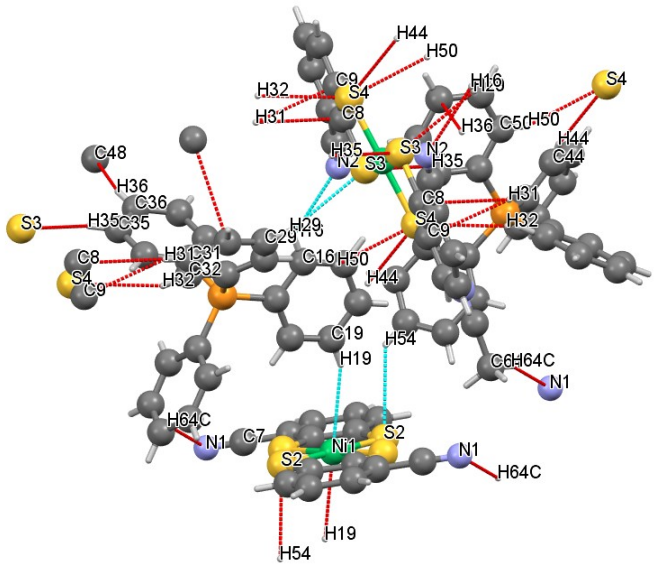


Table SM7: Short contacts list of compound **1.CH_3CN**

	Short Contacts	Symmetry operation (*)	Length (Å)	Length-∑VdW (Å)	
anion-solvent	C64-H64…N1-C7	2-x,1-y,-z	2.676	-0.074	C-H…N≡C
cation- cation	C30…C30	1-x,-y,1-z	3.301	-0.099	π…π
	C36-H36…C48	-1+x,y,z	2.832	-0.068	C-H…π
anion-cation	Ni1…H19-C19	x,y,z	2.759	-0.071	
	S2…H54	1-x,1-y,-z	2.956	-0.044	
	S3…H29	x,y,z	2.959	-0.041	
	S3…H35	1+x,y,z	2.825	-0.175	
	S4…H32	1-x,-y,1-z	2.825	-0.175	
	S4…H44	2-x,1-y,1-z	2.728	-0.272	
	S4…H50	2-x,1-y,1-z	2.699	-0.301	
	C16-H16…N2-C14	x,y,z	2.644	-0.106	C-H…N≡C
	C31-H31…C8	1-x,-y,1-z	2.821	-0.079	C-H…π
	C31-H31…C9	1-x,-y,1-z	2.695	-0.205	C-H…π

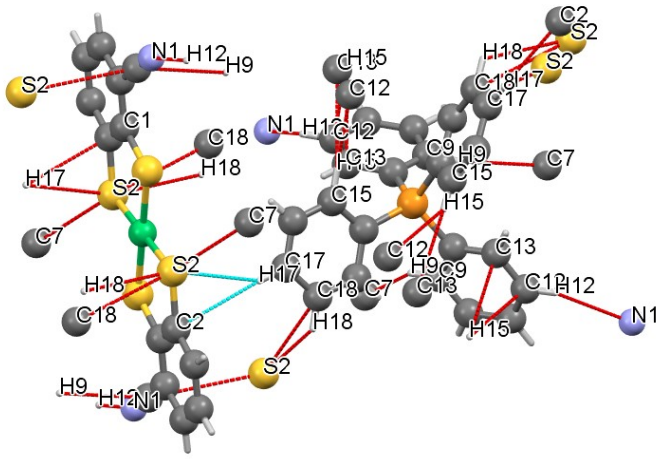


Table SM8: Short contact list of compound **2-α**

	Short Contacts	**Symmetry operation (*)**	**Length (Å)**	**Length-∑VdW (Å)**	
anion-anion	S2…C7	1/2-x,-1/2+y,1/2-z	3.582	0.082	
	C3…C4		3.510	0.110	
cation- cation	C15-H15…C12	x,1-y,-1/2+z	2.934	0.034	C-H…π*2
	C15-H15…C13	x,1-y,-1/2+z	2.981	0.081	C-H…π*2
anion-cation	S2…H17	x,y,z	2.949	-0.051	
	S2…H18	1/2-x,-1/2+y,1/2-z	2.962	-0.038	
	C12-H12…N1-C7	-1/2+x,1.5-y,1/2+z	2.776	0.026	C-H…N≡C

*2 aromatic CH/pi hydrogen bonds; edge-to-face; T-shape aromatic interaction

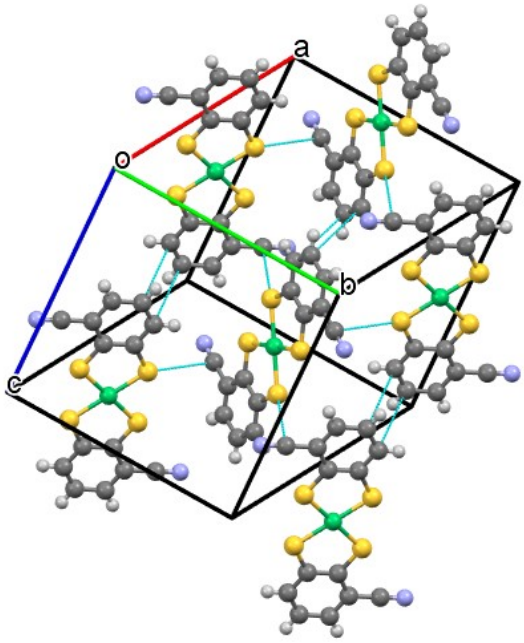


Figure SM11. Structural detail of the C···C and C···S interactions in the **2-α** anionic layer.

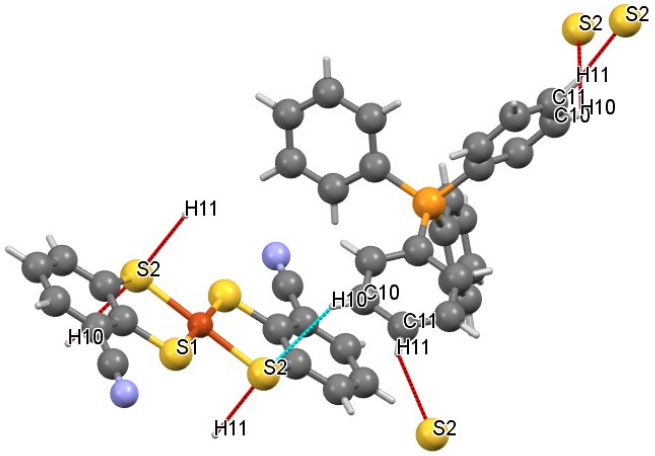


Table SM9: Short contacts list of compound **4-α**

	Short Contacts	Symmetry operation (*)	Length(Å)	Length-∑VdW (Å)	
anion-anion	S2…C7	½-x,-1/2+y,1/2-z	3.562	0.062	
	C3…C4	½-x,1.5-y,-z	3.496	0.096	
cation- cation	C13-H13…C15	-x,y,1.5-z	2.973	0.073	C-H…π*2
	C13-H13…C16	-x,y,1.5-z	0.918	0.018	C-H…π*2
anion-cation	S2…H11	x,1-y,-1/2+z	2.955	-0.045	
	S2…H10	½-x,1.5-y,1-z	2.961	-0.039	
	S2…C10	x,y,z	3.546	0.046	
	C16-H16…N1-C7	-1/2+x,1/2+y,z	2.792	0.042	C-H…N≡C

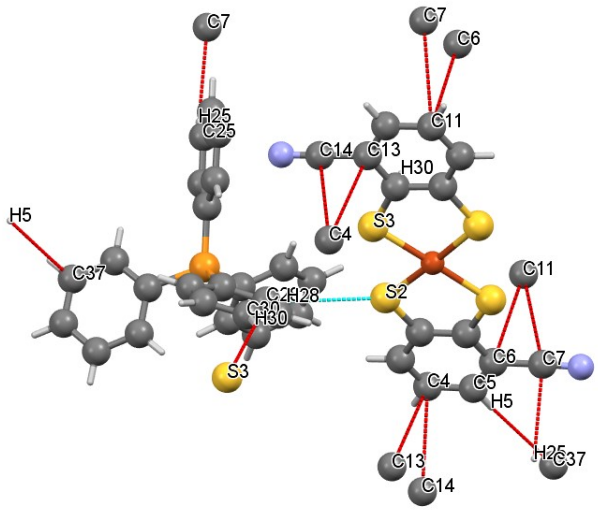


Table SM10: Short contacts list of compound **4- β**

	Short Contacts	Symmetry operation (*)	Length(Å)	Length-∑VdW(Å)	
anion-anion	C4-C13	1-x,-1/2+y,1-z	3.349	-0.051	π…π
	C4-C14	1-x,-1/2+y,1-z	3.349	-0.051	π…π
	C6-C11	2-x,-1/2+y,1-z	3.302	-0.098	π…π
	C7-C11	2-x,-1/2+y,1-z	3.374	-0.026	π…π
anion-cation	S2…H28	x,y,z	2.933	-0.067	
	S3…H30	1+x,y,1+z	2.995	-0.005	
	C25-H25…C7	x,y,1+z	2.860	-0.040	C-H…π
	C5-H5…C37	1+x,y,1+z	2.857	-0.043	C-H…π

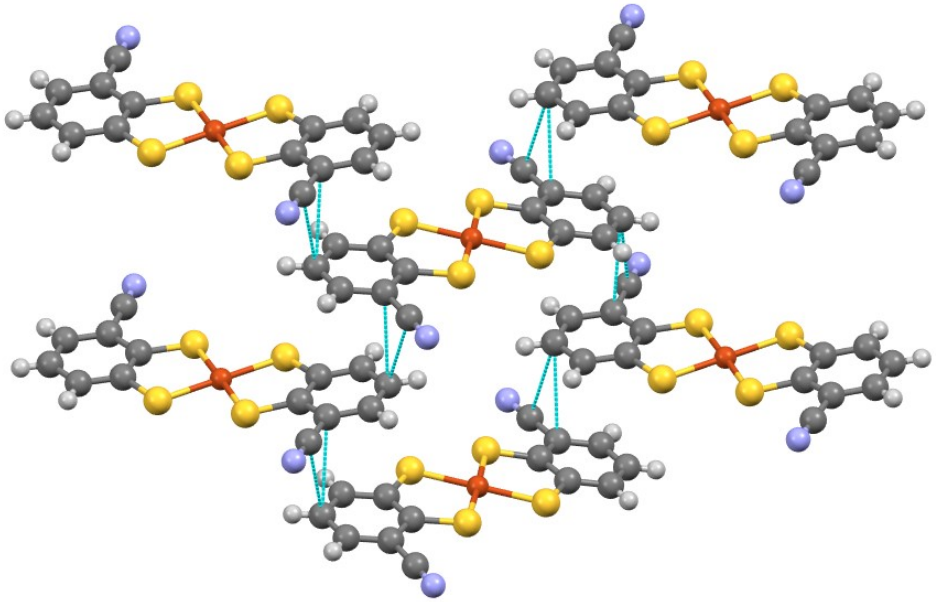


Figure SM12. Structural detail of the C···C interactions in the **β-4** anionic layer.