Electronic Supplementary Material (ESI) for Dalton Transactions

Enhancing σ/π-type Copper(I)···thiophene Interactions by Metal Doping (Metal = Li, Na, K, Ca, Sc)

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Table S1 Calculated interaction energies and BSSE energies of π-type $C_4H_4S\cdots CuX$ and $MC_4H_4S\cdots CuX$ (M = Li, Na, K; X = F, Cl, Br) at different levels

	MP2/6-311+G(2df)	CCSD/6-311+G(2df)	wB97xd/6-311+G(2df)	wb97xd/aug-cc-pVDZ
$LiC_4H_4S\cdots CuF$	-169.9(22.7)	-135.6(4.6)	-138.9(5.1)	-152.7
LiC4H4S···CuCl	-158.5(22.7)	-131.7(4.5)	-162.4(5.1)	-142.8
LiC4H4S···CuBr	-154.9(22.2)	-129.3(4.4)	-154.6(4.6)	-139.2
NaC4H4S···CuF	-175.7(22.4)	-146.3(4.5)	-151.8(5.1)	-166.0
NaC4H4S···CuCl	-165.6(22.4)	-143.5(4.4)	-169.3(5.0)	-157.4
NaC4H4S···CuBr	-165.0(21.9)	-141.4(4.3)	-159.8(4.5)	-154.0
$KC_4H_4S\cdots CuF$	-188.2(22.8)	-155.9(4.7)	-156.4(5.1)	-177.8
$KC_4H_4S\cdots CuCl$	-178.9(23.0)	-153.6(4.6)	-138.9(5.1)	-170.0
$KC_4H_4S\cdots CuBr$	-176.0(22.7)	-152.0(4.6)	-162.4(4.6)	-166.8

The values in parentheses are BSSE energies.

Table *S*2 NBO bond orbital coefficients of π-type complexes

Complexs	Orbital coefficients	d contribution(%)
$LiC_4H_4S\cdots CuX$	No BD(C-Li)	0.00
$NaC_4H_4S\cdots CuX$	No BD(C-Na)	0.00
$KC_4H_4S\cdots CuX$	No BD(C-K)	0.00
$CaC_4H_4S\cdots CuF$	BD(C-Ca)=0.9094C(8.05%s+91.80%p)+0.4160Ca(40.49%s+ 14.64%p+44.86%d)	7.76
$CaC_4H_4S\cdots CuCl$	BD(C-Ca)=0.9083C(7.53%s+92.32%p)+0.4182Ca(40.75%s+14.93%p+44.31%d)	7.75
$CaC_4H_4S\cdots CuBr$	BD(C-Ca)=0.9081C(7.97%s+91.85%p)+0.4188Ca(40.86%s+ 15.02%p+44.11%d)	7.74
$ScC_4H_4S\cdots CuF$	BD(C2-Sc)=0.8272C(13.53%s+86.31%p)+0.5619Sc(21.38%s+3.48%p+75.11%d)	23.7
	BD(C3--Sc)=0.7519C(0.02%s+99.86%p)+0.6593Sc(4.47%s+2.86%p+92.65%d)	40.3
$ScC_4H_4S\cdots CuCl$	BD(C2-Sc)=0.8282C(13.45%s+86.39%p)+ 0.5604Sc(19.28%s+3.48%p+77.20%d)	24.2
	BD(C3-Sc)=0.7618C(0.01%s+99.87%p)+ 0.6478Sc(3.732%s+2.85%p+93.39%d)	39.2
$ScC_4H_4S\cdots CuBr$	BD(C2-Sc)=0.8287C(13.46%s+86.38%p)+0.5597Sc(18.45%s+3.59%p+77.93%d)	24.4
	BD(C3-Sc)=0.7652C(0.02%s+99.84%p)+0.6438Sc(3.49%s+2.91%p+93.59%d)	38.8

X=F, Cl, and Br

Table S3 Topological properties at the BCP of Cu···S in σ-type C4H4S···CuX and MC4H4S···CuX (M = Li, Na, K, Ca, Sc; X = F, Cl, Br) (all values in a. u.)

Complexes	$\rho(r_c)$	$\nabla^2\rho(r_c)$	G_c	V_c	H_c	$-G_c/V_c$	$\delta(Cu, S)$
$C_4H_4S\cdots CuF$	0.0928	0.2577	0.0954	-0.1264	-0.0310	0.7547	0.7678
$C_4H_4S\cdots CuCl$	0.0864	0.2326	0.0864	-0.1147	-0.0283	0.7533	0.7036
$C_4H_4S\cdots CuBr$	0.0847	0.2247	0.0838	-0.1114	-0.0276	0.7522	0.6875
$LiC_4H_4S\cdots CuF$	0.0949	0.2352	0.0939	-0.1289	-0.0350	0.7285	0.7889
$LiC_4H_4S\cdots CuCl$	0.0887	0.2130	0.0854	-0.1175	-0.0321	0.7268	0.7293
$LiC_4H_4S\cdots CuBr$	0.0873	0.2068	0.0832	-0.1146	-0.0314	0.7260	0.7166
$NaC_4H_4S\cdots CuF$	0.0948	0.2356	0.0937	-0.1285	-0.0348	0.7292	0.7916
$NaC_4H_4S\cdots CuCl$	0.0890	0.2145	0.0857	-0.1178	-0.0321	0.7275	0.7353
$NaC_4H_4S\cdots CuBr$	0.0877	0.2086	0.0836	-0.1151	-0.0315	0.7263	0.7225
$KC_4H_4S\cdots CuF$	0.0952	0.2383	0.0944	-0.1293	-0.0349	0.7301	0.7991
$KC_4H_4S\cdots CuCl$	0.0896	0.2169	0.0864	-0.1187	-0.0323	0.7279	0.7422
$KC_4H_4S\cdots CuBr$	0.0882	0.2108	0.0843	-0.1159	-0.0316	0.7274	0.7295
$CaC_4H_4S\cdots CuF$	0.0968	0.2477	0.0971	-0.1322	-0.0351	0.7345	0.8193
$CaC_4H_4S\cdots CuCl$	0.0915	0.2275	0.0895	-0.1220	-0.0325	0.7336	0.7652
$CaC_4H_4S\cdots CuBr$	0.0901	0.2212	0.0873	-0.1192	-0.0319	0.7324	0.7520
$ScC_4H_4S\cdots CuF$	0.0964	0.2515	0.0979	-0.1330	-0.0351	0.7361	0.8049
$ScC_4H_4S\cdots CuCl$	0.0904	0.2293	0.0895	-0.1218	-0.0323	0.7348	0.7465
$ScC_4H_4S\cdots CuBr$	0.0890	0.2234	0.0874	-0.1189	-0.0315	0.7351	0.7333

Table *S*4 Atomic net charge on different regions of σ-type $C_4H_4S\cdots CuX$ and $MC_4H_4S\cdots CuX$ (M = Li, Na, K, Ca, Sc; X = F, Cl, Br)

	M	Cu	X	CuX	thiophene
$C_4H_4S\cdots CuF$		0.6182	-0.7508	-0.1326	0.1326
$C_4H_4S\cdots CuCl$		0.5189	-0.6549	-0.1360	0.1360
$C_4H_4S\cdots CuBr$		0.4686	-0.6044	-0.1358	0.1358
$LiC_4H_4S\cdots CuF$	0.9665	0.5745	-0.7559	-0.1814	-0.7851
$LiC_4H_4S\cdots CuCl$	0.8075	0.4845	-0.6696	-0.1851	-0.6224
$LiC_4H_4S\cdots CuBr$	0.9601	0.4347	-0.6210	-0.1863	-0.7738
$NaC_4H_4S\cdots CuF$	0.8944	0.5683	-0.7593	-0.1910	-0.7034
$NaC_4H_4S\cdots CuCl$	0.8950	0.4810	-0.6761	-0.1951	-0.6999
$NaC_4H_4S\cdots CuBr$	0.8951	0.4324	-0.6289	-0.1965	-0.6986
$KC_4H_4S\cdots CuF$	0.8824	0.5656	-0.7614	-0.1958	-0.6866
$KC_4H_4S\cdots CuCl$	0.8839	0.4799	-0.6797	-0.1998	-0.6841
$KC_4H_4S\cdots CuBr$	0.8839	0.4319	-0.6332	-0.2013	-0.6826
$CaC_4H_4S\cdots CuF$	1.3986	0.5614	-0.7630	-0.2016	-1.1970
$CaC_4H_4S\cdots CuCl$	1.4030	0.4768	-0.6832	-0.2064	-1.1966
$CaC_4H_4S\cdots CuBr$	1.4066	0.4293	-0.6379	-0.2086	-1.1980
$ScC_4H_4S\cdots CuF$	1.2985	0.5740	-0.7587	-0.1847	-1.1138
$ScC_4H_4S\cdots CuCl$	1.3036	0.4873	-0.6752	-0.1879	-1.1157
$ScC_4H_4S\cdots CuBr$	1.3043	0.4392	-0.6277	-0.1885	-1.1158

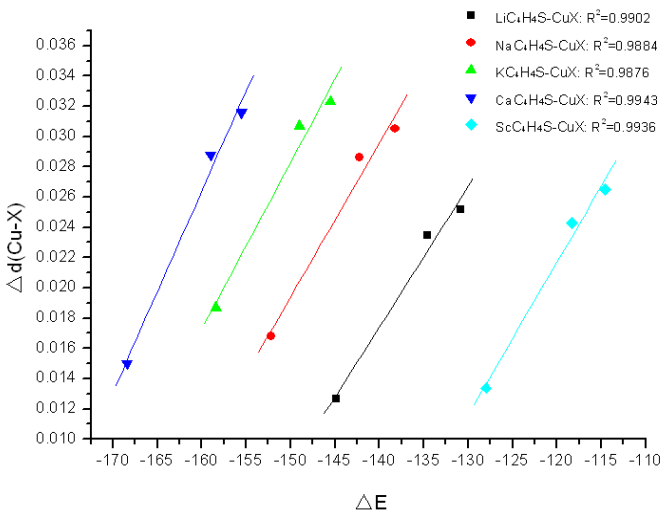
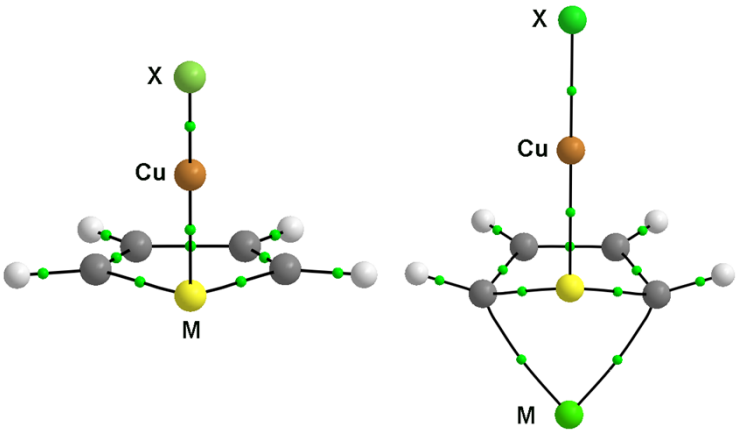


Figure S1 Linear relationships between interaction energy(Δ*E*) and the bond lengths changes of Cu···X bonding(Δ*d*(Cu-X)) in σ-type C_4H_4S···CuX.



(a) (b)

Figure S2 Molecule graphs of electron density of σ-type $C_4H_4S\cdots CuX$(a) and $MC_4H_4S\cdots CuX$(b) (M = Li, Na, K, Ca, Sc; X = F, Cl, Br).

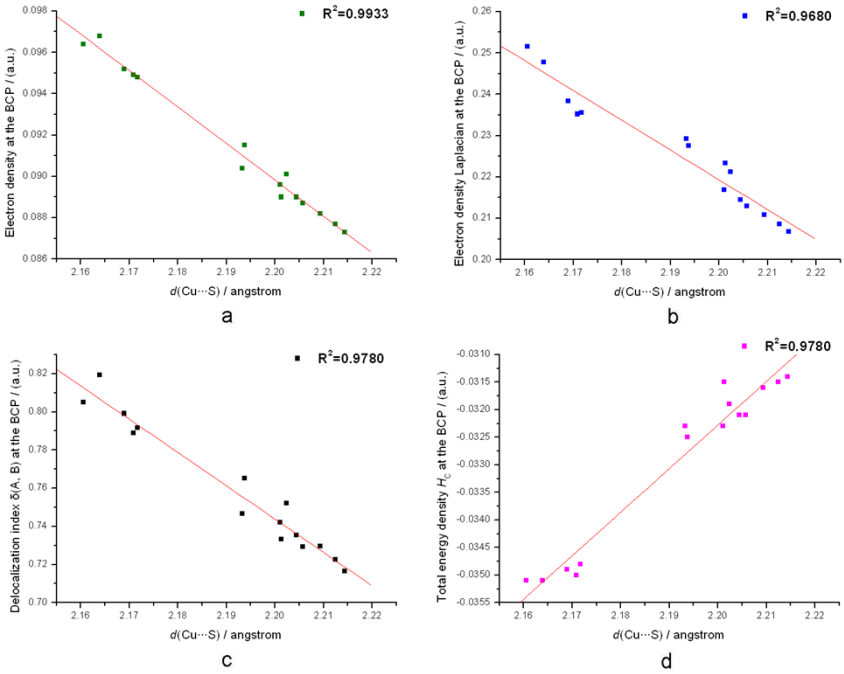


Figure S3 Linear relationships between topological properties at the BCPs and the bond lengths d(Cu···S) of Cu··S bonding in σ-type MC_4H_4S···CuX (M = Li, Na, K, Ca, Sc; X = F, Cl, Br). (a) Electron density $\rho(r_c)$ and the bond lengths, (b) Electron density Laplacian $\nabla^2\rho(r_c)$ and the bond lengths, (c) Delocalization index $\delta(A, B)$ and the bond lengths, (d) Total energy density H_c and the bond lengths.

Relationship between the topological parameters and Cu···S bond lengths

$$\rho(r_c) = 0.4778 - 0.1764 \times d(\mathrm{Cu}\cdots\mathrm{S})$$

$$\nabla^2\rho(r_c) = 1.8043 - 0.7205 \times d(\mathrm{Cu}\cdots\mathrm{S})$$

$$\delta(A, B) = 4.5825 - 1.7449 \times d(\mathrm{Cu}\cdots\mathrm{S})$$

$$H_c = -0.2062 + 0.0791 \times d(\mathrm{Cu}\cdots\mathrm{S})$$

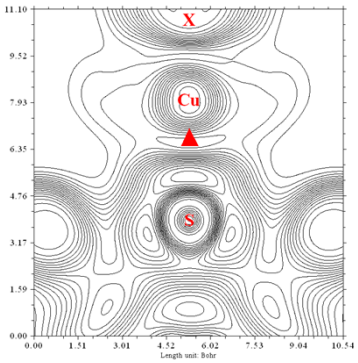


Figure S4 Two-dimensional (2D) cross sections ELF through the σ-type $MC_4H_4S\cdots CuX$ (M = Li, Na, K, Ca, Sc; X = F, Cl, Br).

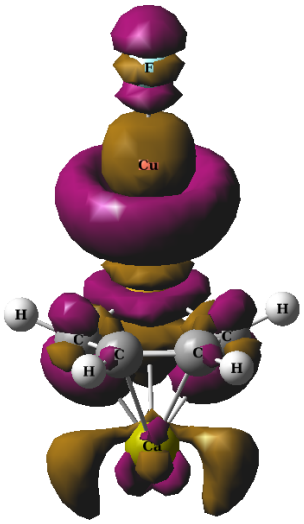


Figure S5 The molecular formation density difference of σ-type $MC_4H_4S\cdots CuX$ (brown is negative, purple is positive and the isosurface is 0.001).