Supporting information

Table S1 Second-order perturbation energy (E^2, kcal/mol) in the dyads at the HF/aug-cc-pVTZ(PP) level.

metal-π	$E^2(1)$	$E^2(2)$	XB	$E^2(3)$
FCCF···CuCCCl	236.62	74.72	CuCCCl···NCH	0.92
FCCF···CuCCBr	237.68	74.52	CuCCBr···NCH	2.28
FCCF···CuCCI	236.60	74.33	CuCCI···NCH	4.14
FCCF···AgCCCl	183.31	47.86	AgCCCl···NCH	0.90
FCCF···AgCCBr	181.97	47.63	AgCCBr···NCH	2.22
FCCF···AgCCI	179.50	47.48	AgCCI···NCH	4.14
FCCF···AuCCCl	408.93	98.11	AuCCCl···NCH	1.10
FCCF···AuCCBr	400.74	97.49	AuCCBr···NCH	2.65
FCCF···AuCCI	392.25	97.2	AuCCI···NCH	4.87
FCCF···LiCCCl	10.50	---	LiCCCl···NCH	0.65
FCCF···LiCCBr	10.66	---	LiCCBr···NCH	1.77
FCCF···LiCCI	10.72	---	LiCCI···NCH	3.33

Note: $E^2(1)$, $E^2(2)$, and $E^2(3)$ correspond to the orbital interactions of $\pi_{C\equiv C}\rightarrow\sigma^*_{C\text{-}M}$ (for Au and Li systems it is $\pi_{C\equiv C}\rightarrow Lp^*_M$), $Lp_M\rightarrow\pi^*_{C\equiv C}$, and $Lp_N\rightarrow\sigma^*_{C\text{-}X}$, respectively.

Table S2 Energy components and interaction energy (kcal/mol) in the dyads at the MP2/aug-cc-pVTZ level

	ES	EX	REP	POL	DISP	INT
FCCF···CuCCCl	-75.08	-123.72	249.04	-65.96	-43.40	-59.12
FCCF···CuCCBr	-75.20	-123.95	249.62	-66.02	-43.45	-59.00
FCCF···CuCCI	-75.17	-123.97	249.71	-66.02	-43.44	-58.89
FCCF···AgCCCl	-67.96	-124.96	247.47	-57.45	-27.88	-30.78
FCCF···AgCCBr	-67.86	-124.80	247.21	-57.35	-27.89	-30.69
FCCF···AgCCI	-67.75	-124.89	246.89	-57.25	-27.87	-30.87
FCCF···AuCCCl	-80.27	-167.66	332.96	-115.78	-25.57	-56.32
FCCF···AuCCBr	-80.07	-167.26	332.24	-115.42	-25.58	-56.09
FCCF···AuCCI	-79.91	-167.07	331.87	-115.23	-25.50	-55.84
FCCF···LiCCCl	-1.80	-1.86	5.03	-4.22	-0.43	-3.28
FCCF···LiCCBr	-1.82	-1.89	5.13	-4.29	-0.43	-3.30
FCCF···LiCCI	-1.82	-1.90	5.15	-4.32	-0.44	-3.33
CuCCCl···NCH	-0.82	-3.27	5.52	-0.53	-2.02	-1.12
CuCCBr···NCH	-2.24	-5.69	9.71	-0.97	-2.66	-1.85
CuCCI···NCH	-4.45	-9.39	16.11	-1.86	-3.27	-2.86
AgCCCl···NCH	-0.68	-3.22	5.42	-0.52	-1.97	-0.97
AgCCBr···NCH	-2.07	-5.61	9.55	-0.95	-2.61	-1.69
AgCCI···NCH	-4.30	-9.37	16.06	-1.84	-3.22	-2.67
AuCCCl···NCH	-1.42	-3.74	6.37	-0.63	-2.20	-1.62
AuCCBr···NCH	-3.00	-6.42	11.06	-1.14	-2.90	-2.40
AuCCI···NCH	-5.42	-10.49	18.16	-2.20	-3.56	-3.51
LiCCCl···NCH	0.00	-2.45	4.07	-0.42	-1.45	-0.25
LiCCBr···NCH	-1.21	-4.59	7.70	-0.75	-2.01	-0.86
LiCCI···NCH	-3.14	-7.75	13.11	-1.45	-2.50	-1.73

Table S3 Changes of equilibrium distances (ΔR, Å) and electron densities ($\Delta\rho$, au) at the intermolecular BCPs in the triads relative to the dyads[a]

complexes	$\Delta R_{M\cdots\pi}$	$\Delta R_{X\cdots N}$	$\Delta\rho_{M\cdots\pi}$	$\Delta\rho_{X\cdots N}$
FCCF···CuCCCl···NCH	0.0014	-0.0293	-0.0004	0.0005
FCCF···CuCCBr···NCH	0.0015	-0.0246	-0.0004	0.0006
FCCF···CuCCI···NCH	0.0018	-0.0241	-0.0005	0.0007
FCCF···AgCCCl···NCH	-0.0046	-0.0169	0.0008	0.0003
FCCF···AgCCBr···NCH	-0.0045	-0.0123	0.0008	0.0003
FCCF···AgCCI···NCH	-0.0046	-0.0092	0.0008	0.0003
FCCF···AuCCCl···NCH	0.0000	-0.0016	-0.0001	0.0001
FCCF···AuCCBr···NCH	-0.0004	0.0052	0.0001	-0.0001
FCCF···AuCCI···NCH	-0.0002	0.0107	0.0000	-0.0003
FCCF···LiCCCl···NCH	0.0028	0.0095	0.0000	-0.0001
FCCF···LiCCBr···NCH	0.0034	0.0122	-0.0001	-0.0002
FCCF···LiCCI···NCH	0.0027	0.0062	-0.0001	-0.0001

[a] BCPs correspond to the M···C in the coinage-metal-π interaction, the Li···π in the lithium bond, and the X···N in the halogen bond.

Table S4 The most positive MEP on the halogen atom ($V_{X,max}$, a.u.) in the dyad FCCF···MCCX and on the metal atom ($V_{M,max}$, a.u.) in the dyad MCCX···NCH as well as their changes (ΔV, a.u.) relative to the molecules.

	$V_{X,max}$	$\Delta V_{X,max}$		$V_{M,max}$	$\Delta V_{M,max}$
FCCF···CuCCCl	0.0249	0.0081	CuCCCl···NCH	0.1664	-0.0064
FCCF···CuCCBr	0.0327	0.0076	CuCCBr···NCH	0.1663	-0.0069
FCCF···CuCCI	0.0440	0.0073	CuCCI···NCH	0.1655	-0.0077
FCCF···AgCCCl	0.0179	0.0034	AgCCCl···NCH	0.1221	-0.0058
FCCF···AgCCBr	0.0260	0.0031	AgCCBr···NCH	0.1221	-0.0064
FCCF···AgCCI	0.0372	0.0029	AgCCI···NCH	0.1222	-0.0064
FCCF···AuCCCl	0.0268	0.0011	AuCCCl···NCH	0.1443	-0.0078
FCCF···AuCCBr	0.0348	0.0007	AuCCBr···NCH	0.1431	-0.0088
FCCF···AuCCI	0.0460	0.0002	AuCCI···NCH	0.1402	-0.0106
FCCF···LiCCCl	-0.0013	-0.0023	LiCCCl···NCH	0.3123	-0.0067
FCCF···LiCCBr	0.0249	0.0081	LiCCBr···NCH	0.1664	-0.0066
FCCF···LiCCI	0.0327	0.0076	LiCCI···NCH	0.1663	-0.0068

Table S5 Second-order perturbation energy (E^2, kcal/mol) of $Lp_N \rightarrow \sigma^*_{C\text{-}X}$ orbital interaction in the triads and its change (ΔE^2, kcal/mol) compared with dyads at the HF/aug-cc-pVTZ(PP) level.

complexes	E^2	ΔE^2
FCCF···CuCCCl···NCH	1.03	0.11
FCCF···CuCCBr···NCH	2.49	0.21
FCCF···CuCCI···NCH	4.65	0.51
FCCF···AgCCCl···NCH	0.95	0.05
FCCF···AgCCBr···NCH	2.32	0.10
FCCF···AgCCI···NCH	4.20	0.06
FCCF···AuCCCl···NCH	1.10	0.00
FCCF···AuCCBr···NCH	2.61	-0.04
FCCF···AuCCI···NCH	4.62	-0.25
FCCF···LiCCCl···NCH	0.62	-0.03
FCCF···LiCCBr···NCH	1.69	-0.08
FCCF···LiCCI···NCH	3.20	-0.13

Table S6 Binding distance (R, Å) and interaction energy (ΔE, kcal/mol) in the dyads.

dyads	ΔE	R	dyads	ΔE	R
HCCH···CuCCCl	-45.16(-52.10)	1.791	FCCF···CuCCCl	-47.51(-61.71)	1.786
HCCH···CuCCBr	-45.02(-51.96)	1.790	FCCF···CuCCBr	-47.35(-61.56)	1.786
HCCH···CuCCI	-44.88(-51.74)	1.792	FCCF···CuCCI	-47.21(-61.46)	1.785
HCCH···AgCCCl	-29.60(-31.93)	2.082	FCCF···AgCCCl	-25.15(-34.83)	2.001
HCCH···AgCCBr	-29.58(-31.91)	2.083	FCCF···AgCCBr	-25.15(-34.71)	2.002
HCCH···AgCCI	-29.53(-31.84)	2.084	FCCF···AgCCI	-24.99(-34.61)	2.002
HCCH···AuCCCl	-44.32(-49.59)	2.014	FCCF···AuCCCl	-45.64(-59.47)	1.962
HCCH···AuCCBr	-44.16(-49.41)	2.015	FCCF···AuCCBr	-45.44(-59.21)	1.962
HCCH···AuCCI	-43.88(-49.10)	2.016	FCCF···AuCCI	-45.14(-58.93)	1.963
HCCH···LiCCCl	-9.25	2.346	FCCF···LiCCCl	-3.14	2.492
HCCH···LiCCBr	-9.30	2.342	FCCF···LiCCBr	-3.17	2.486
HCCH···LiCCI	-9.35	2.340	FCCF···LiCCI	-3.20	2.485
NCCCCN···CuCCI	-38.43(-47.49)	1.792	---	---	---
NCCCCN···AgCCI	-19.45(-24.05)	2.033	---	---	---
NCCCCN···AuCCI	-36.48(-44.52)	1.990	---	---	---
NCCCCN···LiCCI	2.53(2.39)	2.711	---	---	---

Note: R is the distance between the central point of C≡C and the M in the metal-π interaction. Data in parentheses are the interaction energies obtained with the geometries of monomers frozen in the complexes for HCCH, FCCF, and NCCCCN.

Table S7 The angle of C≡C-Y (α, °) in the dyads and corresponding triads (in parantheses).

dyads	α	dyads	α
HCCH···CuCCCl	161(161)	FCCF···CuCCCl	158(158)
HCCH···CuCCBr	161(161)	FCCF···CuCCBr	158(158)
HCCH···CuCCI	161(161)	FCCF···CuCCI	158(158)
HCCH···AgCCCl	169(169)	FCCF···AgCCCl	162(161)
HCCH···AgCCBr	169(169)	FCCF···AgCCBr	162(161)
HCCH···AgCCI	169(169)	FCCF···AgCCI	162(161)
HCCH···AuCCCl	164(163)	FCCF···AuCCCl	158(158)
HCCH···AuCCBr	164(163)	FCCF···AuCCBr	158(158)
HCCH···AuCCI	164(163)	FCCF···AuCCI	158(158)
HCCH···LiCCCl	178(179)	FCCF···LiCCCl	178(178)
HCCH···LiCCBr	178(179)	FCCF···LiCCBr	178(178)
HCCH···LiCCI	178(179)	FCCF···LiCCI	178(178)
NCCCCN···CuCCI	159(159)	---	---
NCCCCN···AgCCI	165(164)	---	---
NCCCCN···AuCCI	160(160)	---	---
NCCCCN···LiCCI	179(179)	---	---

Fig. S1 The relationship between second-order perturbation energy (E^2, kcal/mol) and interaction energy (ΔE, kcal/mol) for each type of MCCX···NCH interaction with the same metal. M in a-d is Cu, Ag, Au, and Li, respectively.

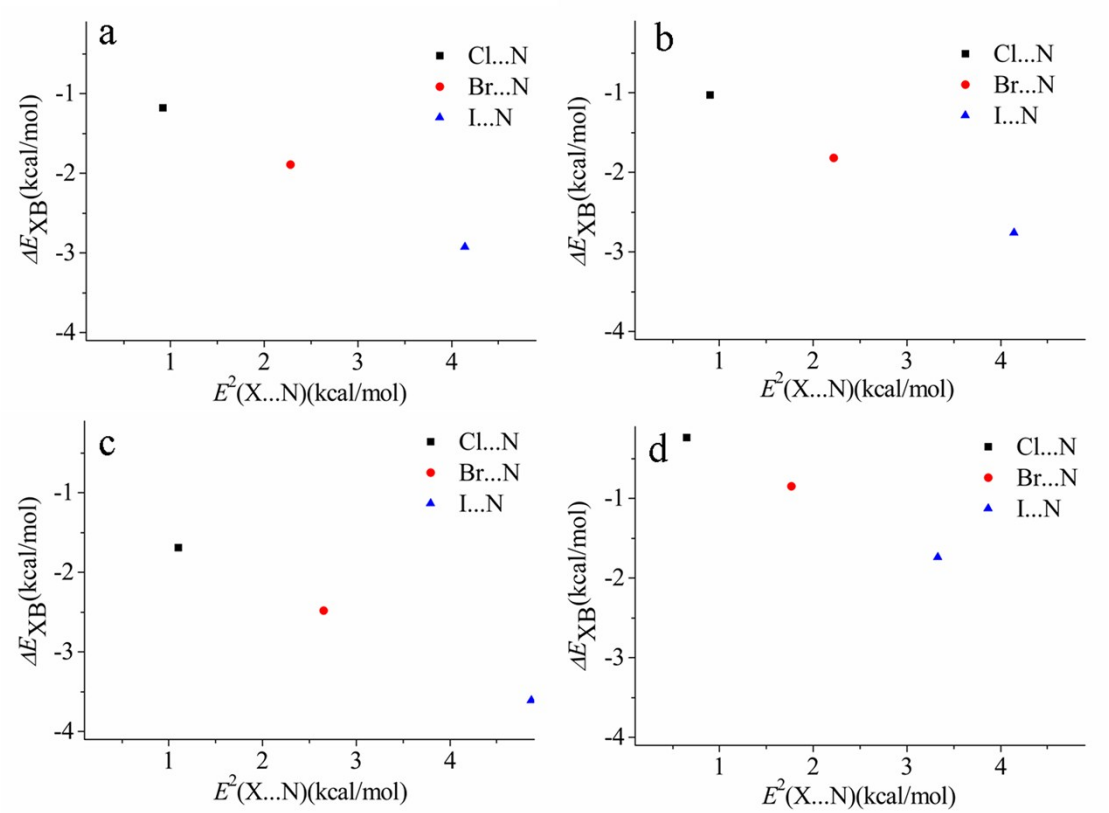

Fig. S2 Electron density difference maps of some dyads and triads. The red lines represent the concentration of charge density and the blue ones are the regions with reduced charge density.