Supplementary Information

Design strategies of two-dimensional metal-organic frameworks toward efficient electrocatalysts for N_2 reduction：Cooperativity of transition metals and organic linkers

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Table S1. Computed lattice constant, bond length (d), bader charge of the metal atom (Q_M, positive values indicate positive charge), d band center and binding energies of metal atom (E_b) for $M_3C_{12}X_{12}$.

structure	lattice /Å	d_{M-X} /Å	d_{X-C} /Å	Q_M/e	d band center	E_b(M) / eV
$Cr_3C_{12}NH_{12}$	13.84	1.97	1.35	1.31	0.305	-7.86
$Cr_3C_{12}O_{12}$	13.44	1.94	1.31	1.43	0.587	-7.53
$Cr_3C_{12}S_{12}$	15.07	2.26	1.73	1.11	0.364	-7.20
$Cr_3C_{12}Se_{12}$	15.76	2.38	1.91	0.97	0.384	-6.67
$Mo_3C_{12}NH_{12}$	14.22	2.05	1.38	1.42	-0.690	-8.45
$Mo_3C_{12}O_{12}$	13.92	1.98	1.33	1.66	-0.779	-8.15
$Mo_3C_{12}S_{12}$	15.46	2.35	1.75	1.17	-0.257	-8.27
$Mo_3C_{12}Se_{12}$	16.14	2.46	1.93	0.97	-0.069	-7.79
$W_3C_{12}NH_{12}$	14.10	2.03	1.40	1.63	-1.381	-10.31
$W_3C_{12}O_{12}$	13.64	1.93	1.36	1.82	-1.629	-9.97
$W_3C_{12}S_{12}$	15.43	2.33	1.76	1.30	-0.380	-10.07
$W_3C_{12}Se_{12}$	16.11	2.46	1.94	1.06	-0.031	-9.48

Table S2. The metal atom binding energies of the experimentally successfully synthesized $M_3C_{12}X_{12}$.

structure	E_b(M) / eV	structure	E_b(M) / eV
$Co_3C_{12}NH_{12}$[1, 2]	-7.01	$Ni_3C_{12}O_{12}$[1, 3]	-7.48
$Co_3C_{12}S_{12}$[1, 4]	-6.61	$Cu_3C_{12}NH_{12}$[1, 2]	-6.65
$Pd_3C_{12}S_{12}$[1, 5]	-6.41	$Cu_3C_{12}O_{12}$[1, 3]	-7.21
$Ni_3C_{12}NH_{12}$[1, 2]	-6.89	$Pt_3C_{12}S_{12}$[6, 7]	-9.31

Table S3. The adsorption free energy of important reactive species in NRR on $M_3C_{12}X_{12}$.

Structure/eV	$G_{ad}(N_2$-end)	Gad(N_2H-end)	$G_{ad}(N_2$-side)	$G_{ad}(N_2H$-side)	$G_{ad}(NH_2)$	$G_{ad}(NH_3)$
$Cr_3C_{12}NH_{12}$	0.07	-1.54	0.35#	--	-0.90	-0.10
$Cr_3C_{12}O_{12}$	0.08	-1.35	0.26#	--	-2.12	-0.68
$Cr_3C_{12}S_{12}$	-0.25	-1.85	0.36#	--	-2.42	-0.94
$Cr_3C_{12}Se_{12}$	-0.20	-1.77	0.23#	--	-2.42	-0.88
$Mo_3C_{12}NH_{12}$	-0.46	-2.40	0.15	-2.16	-2.96	-0.37
$Mo_3C_{12}O_{12}$	-0.21	-2.15	0.35	-1.79	-2.94	-0.75
$Mo_3C_{12}S_{12}$	-0.84	-2.60	-0.30	-2.49	-3.53	-1.62
$Mo_3C_{12}Se_{12}$	-0.98	-2.69	-0.41	-2.54	-3.62	-1.81
$W_3C_{12}NH_{12}$	-0.48	-2.64	-0.23	-2.62	-3.60	-0.32
$W_3C_{12}O_{12}$	-0.28	-2.58	0.02	-2.49	-3.64	-0.86
$W_3C_{12}S_{12}$	-0.78	-2.77	-0.19	-2.61	-3.90	-1.62
$W_3C_{12}Se_{12}$	-0.92	-2.82	-0.28	-2.83	-3.97	-1.80

represents physical adsorption.

Table S4. The Gibbs free energy(Δ G) for the rate-limiting steps of nitrogen reduction reactions and single hydrogen adsorption on $M_3C_{12}X_{12}$.

Structure/eV	$\Delta G(N_2$-N_2H-end)	$\Delta G(N_2$-N_2H-side)	$\Delta G(NH_2$-$NH_3)$	$\Delta G(H)_M$	$\Delta G(H)_X$
$Cr_3C_{12}NH_{12}$	0.95	--	-1.39	0.36	--
$Cr_3C_{12}O_{12}$	1.14	--	-0.74	0.43	0.06
$Cr_3C_{12}S_{12}$	0.97	--	-0.70	0.34	-0.02
$Cr_3C_{12}Se_{12}$	0.99	--	-0.64	0.28	0.14
$Mo_3C_{12}NH_{12}$	0.63	0.26	0.41	-0.47	--
$Mo_3C_{12}O_{12}$	0.62	0.42	0.02	-0.27	0.47
$Mo_3C_{12}S_{12}$	0.80	0.38	-0.27	-0.68	0.16
$Mo_3C_{12}Se_{12}$	0.86	0.44	-0.37	-0.66	0.10
$W_3C_{12}NH_{12}$	0.41	0.18	1.10	-0.92	--
$W_3C_{12}O_{12}$	0.26	0.05	0.60	-0.65	1.14
$W_3C_{12}S_{12}$	0.57	0.15	0.10	-0.95	0.31
$W_3C_{12}Se_{12}$	0.66	0.01	-0.01	-1.00	0.34

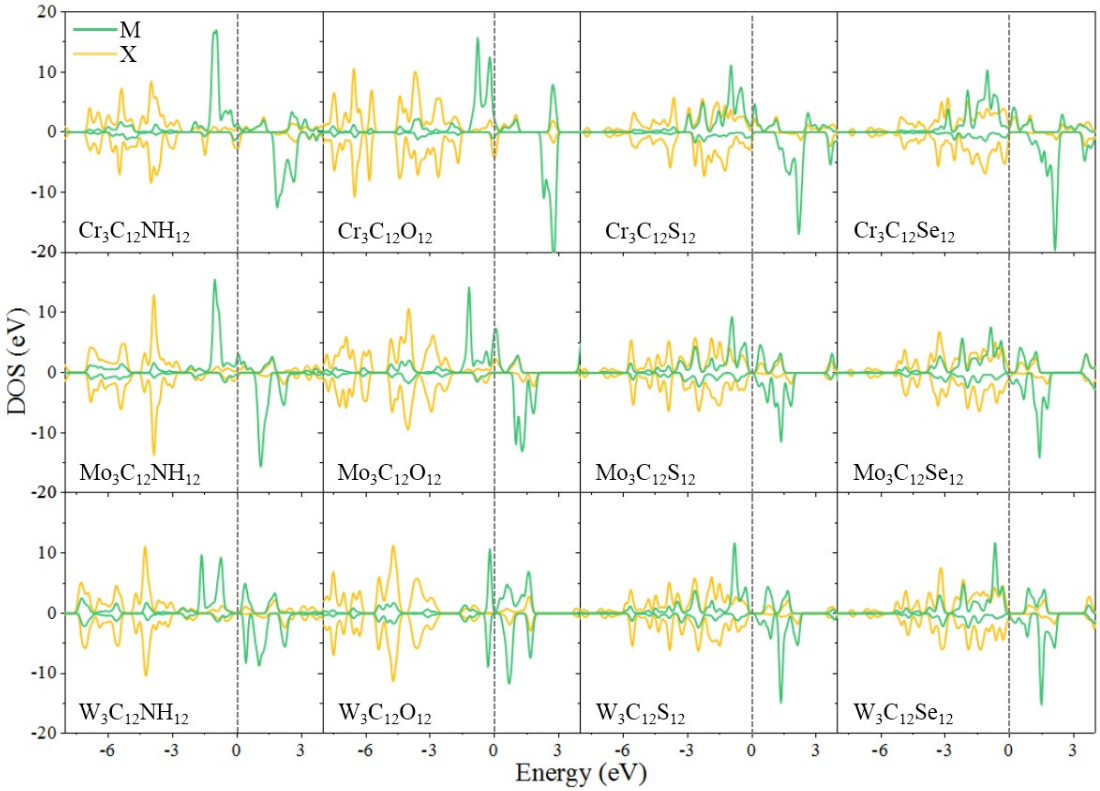

Figure S1. Spin-polarized partial density of states of M-d orbitals and X-p orbitals for $M_3C_{12}X_{12}$. The Fermi level is set to zero.

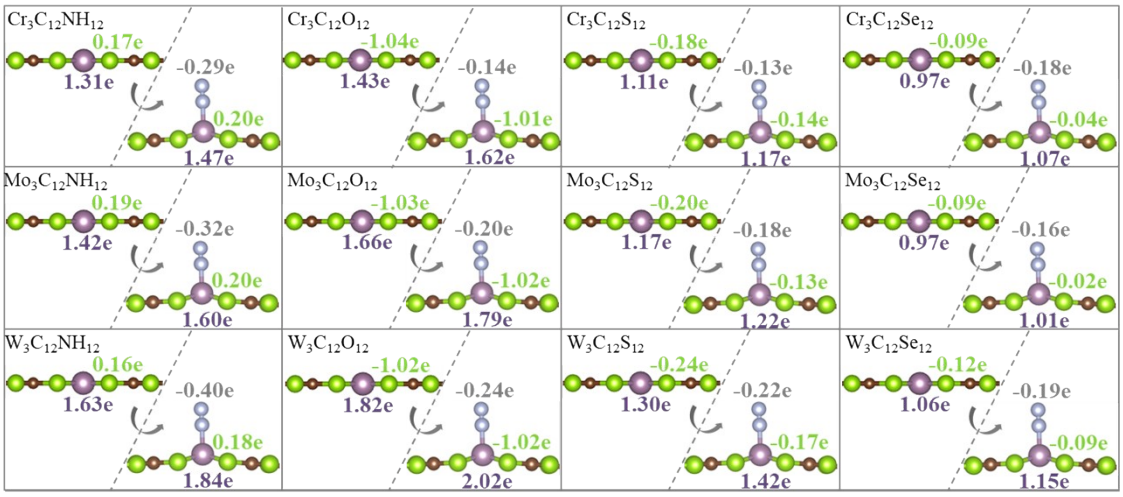

Figure S2. Schematic diagram of Bader charge distribution before and after N_2 adsorption on $M_3C_{12}X_{12}$.

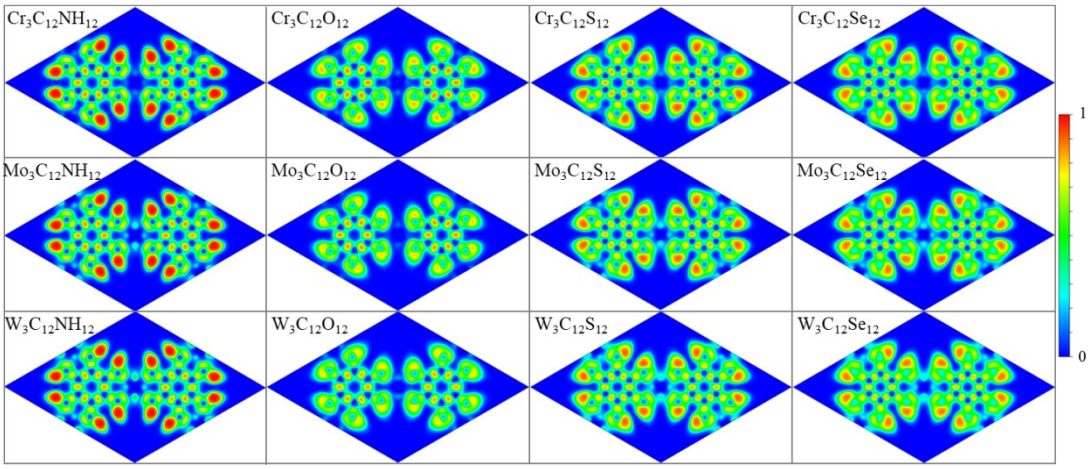

Figure S3. Illustrations of electron localization functions for unit cell $M_3C_{12}X_{12}$.

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