Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Room Temperature O Transfer from N_2O to CO Mediated by Nearest Cd(I) Ions in MFI Zeolite Cavity

Supplementary figures and tables

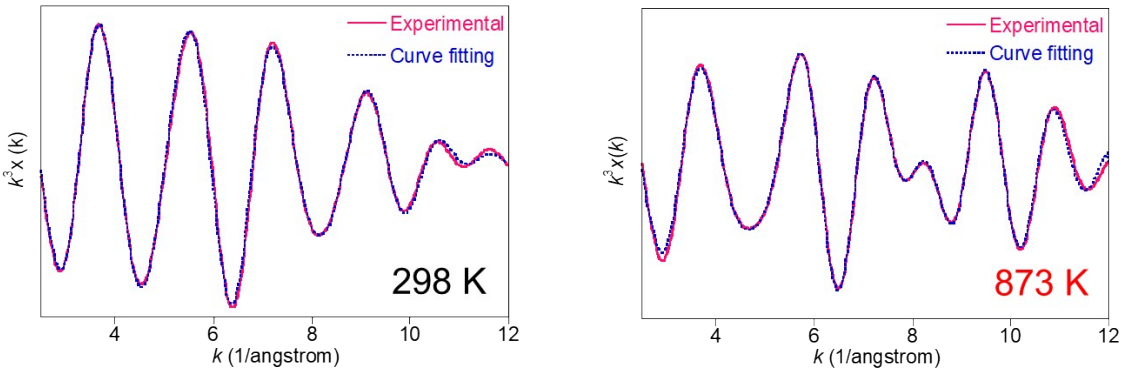

Fig. S1 Comparisons of the Fourier-transformed EXAFS (2< k <12 Å^{-1}) with the curve fitting data: (left) 298 K- and (right) 873 K-evacuated samples.

Table S1 Qualitative EXAFS analysis of Cd–O and Cd–Cd contributions.

	1st (Cd–O)			2nd (Cd–Cd)		
Sample	CN	R [Å]	σ^2 [Å^2]	CN	R [Å]	σ^2 [Å^2]
298 K-evacuated CdMFI	7.0	2.32	0.013	1.1	3.02	0.013
873 K-evacuated CdMFI	3.5	2.27	0.015	**0.9**	**2.67**	0.009

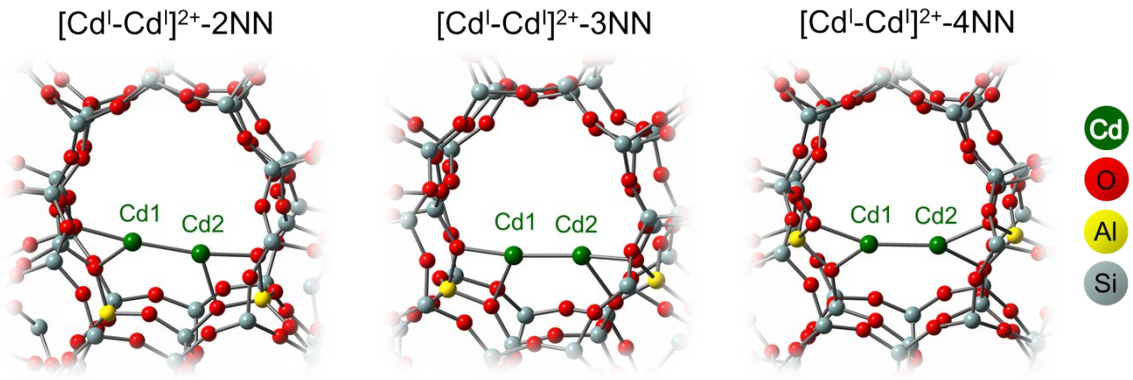

Fig. S2 Optimized [Cd^{I}–Cd^{I}]$^{2+}$-MFI models, i.e., [Cd$_2$]$^{2+}$-[Al$_2$Si$_{90}$O$_{151}$H$_{66}$]$^{2-}$ clusters, having different Al arrays.

Table S2 Selected DFT parameters of the [Cd^{I}–Cd^{I}]$^{2+}$-MFI models shown in Fig. S2: Cd–Cd distance ($R_{Cd1–Cd2}$), natural charge (q_{Cd1}, q_{Cd2}), and σ–σ^* energy ($E_{\sigma–\sigma^*}$).

Sites	$R_{Cd1–Cd2}$ [Å]	q_{Cd1}[a]	q_{Cd2}[a]	$E_{\sigma–\sigma^*}$ [cm^{-1}]
[Cd^{I}–Cd^{I}]$^{2+}$-2NN	2.63	+0.68	+0.75	38250
[Cd^{I}–Cd^{I}]$^{2+}$-3NN	2.63	+0.71	+0.73	40430
[Cd^{I}–Cd^{I}]$^{2+}$-4NN	2.69	+0.72	+0.74	40650

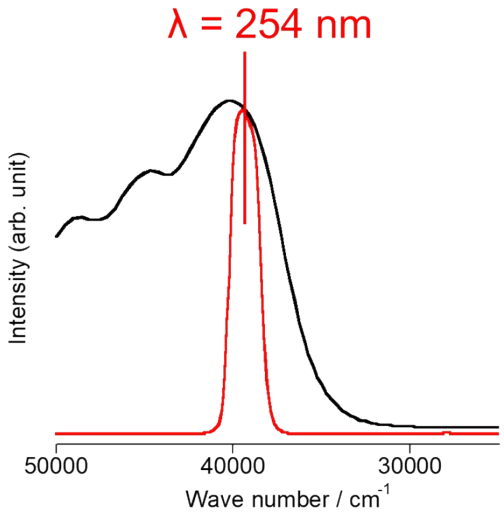

Fig. S3 Energy distributions of the 254 nm light applying to the photoactivation of the Cd^{I}–Cd^{I} bond (red line). For comparison, the UV-vis spectrum of the 873 K-activated CdMFI sample is included (black line). The 254 nm light was generated using a 254 nm band pass filter.

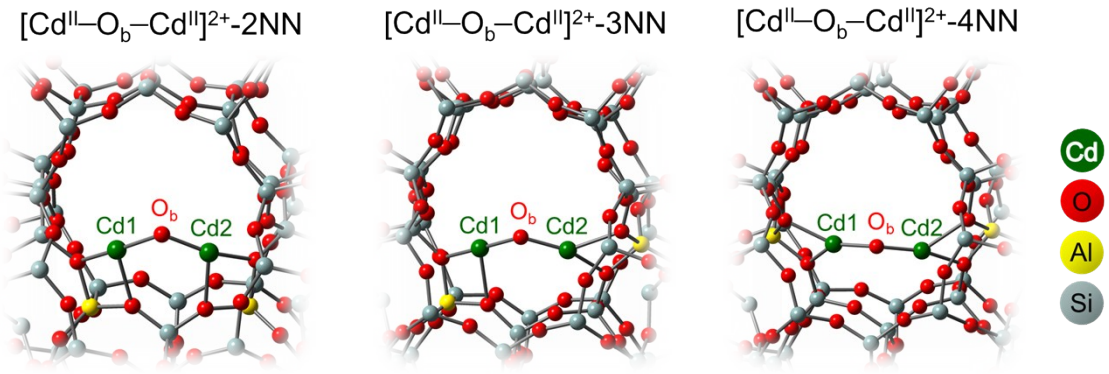

Fig. S4 Optimized $[Cd^{II}–O_b–Cd^{II}]^{2+}$-MFI models, i.e., $[Cd_2O]^{2+}$-$[Al_2Si_{90}O_{151}H_{66}]^{2–}$, having different Al arrays.

Table S3 Selected DFT parameters of the $[Cd^{II}–O_b–Cd^{II}]^{2+}$-MFI models shown in Fig. S4: bond distance ($R_{Cd1–Ob}$, $R_{Cd1–Ob}$, $R_{Cd1–Cd2}$), bond angle (∠Cd–O_b–Cd) natural charge (q_{cd1}, q_{cd2}, q_{Ob}), and LMCT energy (E_{LMCT}).

Sites	$R_{Cd1–Ob}$ [Å]	$R_{Cd2–Ob}$ [Å]	$R_{Cd1–Cd2}$ [Å]	∠Cd–O_b–Cd [°]	q_{Cd1}	q_{Cd2}	q_{Ob}	E_{LMCT} [a] [cm^{-1}]
2NN	2.01	2.02	3.39	114	1.26	1.26	-1.18	40900
3NN	2.01	2.01	3.49	121	1.27	1.30	-1.19	42000
4NN	2.00	2.01	3.60	128	1.31	1.32	-1.21	42400

[a]The most intense peak positions in the UV-vis spectra calculated by TD-DFT are described.

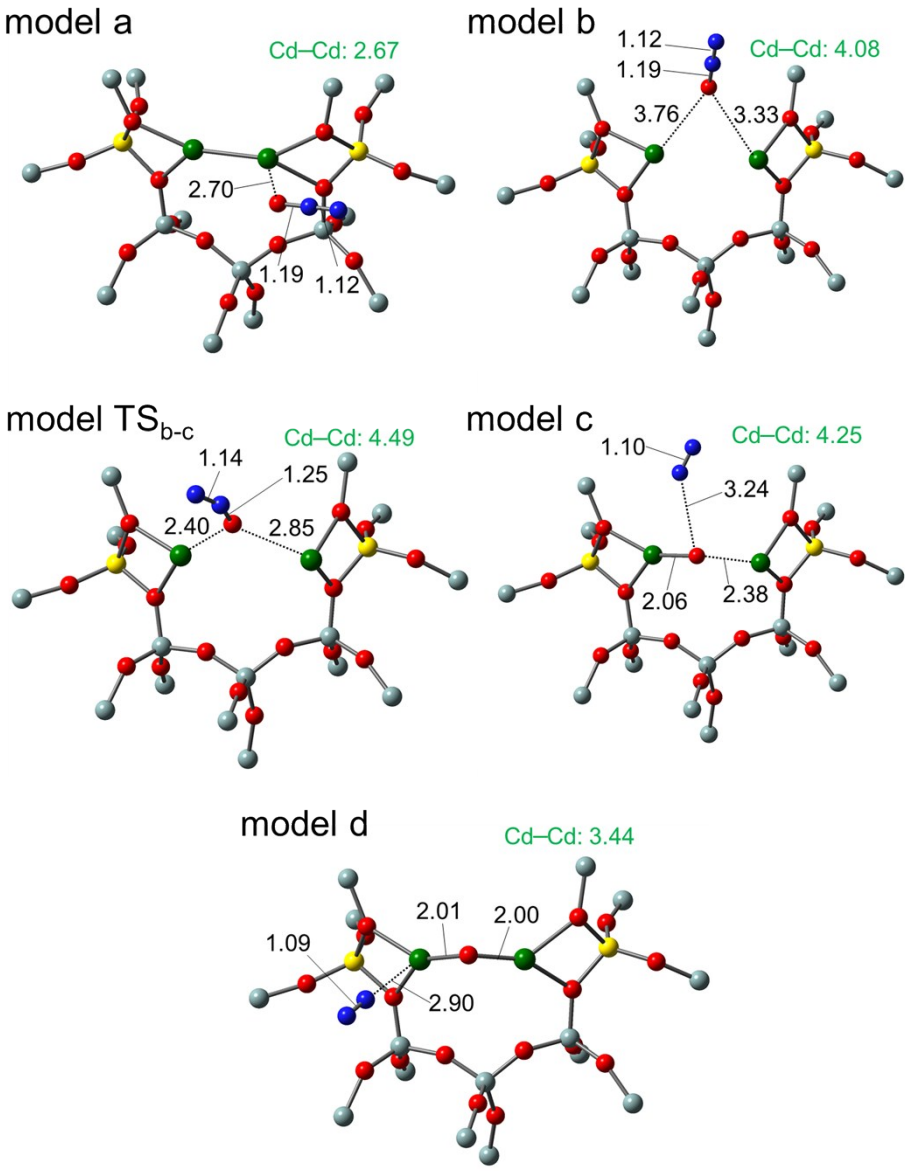

Fig. S5 Structural details of the optimized geometries ($[Cd_2N_2O]^{2+}$-$[Al_2Si_{15}O_{16}H_{36}]^{2-}$, S = 0 or 1) shown in Fig. 8, where terminated H atoms were omitted. Selected bond lengths are given as black and green numbers (Å).

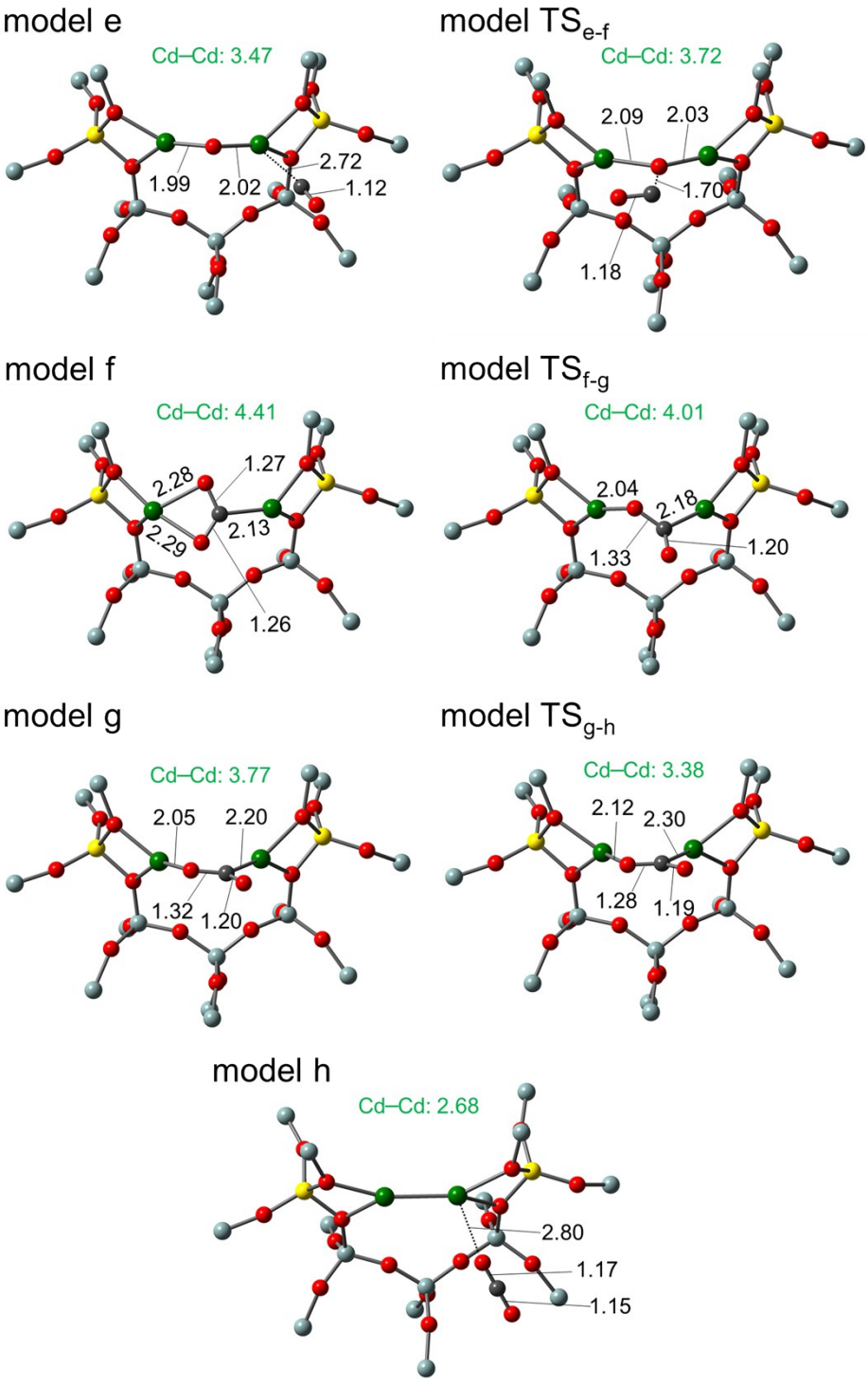

Fig. S6 Structural details of the optimized geometries ($[Cd_2CO_2]^{2+}$-$[Al_2Si_{15}O_{16}H_{36}]^{2-}$, S = 0) shown in Fig. 10, where terminated H atoms were omitted. Selected bond lengths are given as black and green numbers (Å).