Supporting Information for Publication with "Light Induced Charge Transfer from Transition-metal Doped Aluminium Clusters to Carbon Dioxide"

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Table S1 and S2 summarize the convergence parameters that were used in this work.

Tables S3 to S30 contain the lowest energy structures found from our relaxations (results are presented in XYZ-format).

Table 31 shows the structures after adiabatic ionization.

We also provide additional pDOS plots with the DOS being projected onto the atomic orbitals of Al as well as the transition-metal (Figure S1 and S2). All system exhibiting significant back-transfer, $[Al_{12}Ru]-CO_2$, $[Al_{12}Co]-CO_2$ and $[Al_{12}Ni]-CO_2$, show a relatively large

Table S 1: Calculation parameters used for determining the vertical ionization energy ("IP"), adsorption energy, adiabatic ionization energy and most favorable spin-state ("AE") and computation of DOS, pDOS, ELFs, ground-state electron transfer and Casida calculations ("DOS"). "Grid" denotes the spacing of points on the real-space grid while "Box" denotes the radius of the minimum box. In the calculation of the ELF of $[Al_{13}]-CO_2$, a smearing of 0.1 eV was used to achieve convergence.

System	Grid (IP) [Å]	Box (IP)[Å]	Grid (AE) [Å]	Box (AE) [Å]	Grid (DOS) [Å]	Box (DOS) [Å]
$[Al_{12}Zr]-CO_2$	0.18	5	0.06	5	0.16	9
$[Al_{12}Mn]-CO_2$	0.14	6	0.06	5	0.14	9
$[Al_{12}Fe]-CO_2$	0.18	5	0.06	5	0.16	9
$[Al_{12}Ru]-CO_2$	0.20	6	0.06	5	0.18	9
$[Al_{12}Co]-CO_2$	0.16	5	0.06	5	0.14	9
$[Al_{12}Ni]-CO_2$	0.12	5	0.06	5	0.14	9
$[Al_{12}Cu]-CO_2$	0.16	5	0.06	5	0.14	9

Table S 2: Minimal convergence Parameters found for computation of the absorption spectra from time-propagations.

System	Time Step [1/eV]	Grid [Å]	Box Radius [Å]	kick strength [1/Å]
$[Al_{12}Zr]-CO_2$	0.001	0.26	8.0	0.01
$[Al_{12}Mn]-CO_2$	0.001	0.18	8.0	0.01
$[Al_{12}Fe]-CO_2$	0.001	0.22	8.0	0.01
$[Al_{12}Ru]-CO_2$	0.001	0.32	8.0	0.01
$[Al_{12}Co]-CO_2$	0.001	0.20	9.0	0.01
$[Al_{12}Ni]-CO_2$	0.001	0.18	8.0	0.01
$[Al_{12}Cu]-CO_2$	0.001	0.18	13.0	0.01

Table S 3: Coordinates of $[Al_{12}Zr]-CO_2$

System	Atom type	X [Å]	Y [Å]	Z [Å]
$[Al_{12}Zr]-CO_2$	Al	0.00	0.36	0.11
	Zr	0.00	2.53	1.92
	Al	0.00	-0.40	2.70
	Al	1.38	2.47	-0.67
	Al	-1.38	2.47	-0.67
	Al	2.33	0.78	1.28
	Al	-2.33	0.78	1.28
	Al	0.00	1.12	-2.58
	Al	0.00	-2.05	-1.42
	Al	1.44	-1.80	0.93
	Al	-1.44	-1.80	0.93
	Al	2.13	-0.16	-1.34
	Al	-2.13	-0.16	-1.34
	C	0.00	1.35	3.79
	O	0.00	0.28	4.51
	O	0.00	2.58	4.13

Table S 4: Coordinates of $[Al_{12}Mn]-CO_2$

System	Atom type	X [Å]	Y [Å]	Z [Å]
$[Al_{12}Mn]-CO_2$	Al	-0.51	0.00	-0.02
	Mn	-0.39	1.10	2.47
	Al	-0.73	-1.43	2.47
	Al	1.21	2.29	0.90
	Al	-1.61	2.32	0.59
	Al	1.52	-0.23	1.87
	Al	-2.69	0.17	1.49
	Al	0.03	2.27	-1.47
	Al	0.59	0.01	-2.64
	Al	0.81	-2.36	0.48
	Al	-0.51	-2.20	-1.73
	Al	2.20	0.29	-0.59
	Al	-2.19	-2.14	0.27
	C	0.68	2.53	2.96
	O	0.02	2.39	4.02
	O	1.56	3.34	2.50

Table S 5: Coordinates of $[Al_{12}Fe]-CO_2$

System	Atom type	X [Å]	Y [Å]	Z [Å]
$[Al_{12}Fe]-CO_2$	Al	0.47	-0.12	-0.25
	Fe	-0.02	0.87	2.28
	Al	-0.12	-1.65	2.08
	Al	1.76	2.03	0.72
	Al	-1.00	2.23	0.37
	Al	2.29	-0.29	1.73
	Al	-2.00	-0.04	1.21
	Al	0.66	2.17	-1.70
	Al	0.54	-2.30	-2.03
	Al	1.70	-2.48	0.34
	Al	-1.43	-2.15	-0.27
	Al	0.02	-0.01	-3.03
	Al	-2.01	0.38	-1.39
	C	-0.30	3.25	4.51
	O	-0.27	2.08	4.38
	O	-0.32	4.41	4.64

Table S 6: Coordinates of $[Al_{12}Ru]-CO_2$

System	Atom type	X [Å]	Y [Å]	Z [Å]
$[Al_{12}Ru]-CO_2$	Al	0.00	-0.19	0.27
	Ru	0.00	1.10	2.55
	Al	0.00	-2.48	1.56
	Al	1.42	2.12	0.69
	Al	-1.42	2.12	0.69
	Al	2.10	-0.08	2.11
	Al	-2.10	-0.08	2.11
	Al	0.00	1.91	-1.57
	Al	0.00	-0.52	-2.35
	Al	1.36	-2.40	-0.86
	Al	-1.36	-2.40	-0.86
	Al	2.55	-0.15	-0.63
	Al	-2.55	-0.15	-0.63
	C	0.00	3.04	3.27
	O	0.00	2.32	4.31
	O	0.00	4.19	2.90

Table S 7: Coordinates of $[Al_{12}Co]-CO_2$

System	Atom type	X [Å]	Y [Å]	Z [Å]
$[Al_{12}Co]-CO_2$	Al	-0.03	0.00	-0.16
	Co	0.12	1.92	1.77
	Al	-0.12	-0.40	2.71
	Al	1.56	2.11	-0.47
	Al	-1.00	2.67	-0.30
	Al	2.08	0.47	1.49
	Al	-2.06	0.85	1.27
	Al	-1.32	1.05	-2.33
	Al	1.18	0.48	-2.59
	Al	1.16	-2.18	1.04
	Al	-1.51	-1.99	1.13
	Al	2.54	-0.84	-0.81
	Al	-2.65	-0.70	-0.87
	C	0.03	1.58	3.58
	O	-0.11	0.56	4.36
	O	0.12	2.80	3.74

Table S 8: Coordinates of $[Al_{12}Ni]-CO_2$

System	Atom type	X [Å]	Y [Å]	Z [Å]
$[Al_{12}Ni]-CO_2$	Al	0.00	-0.02	0.05
	Ni	0.00	1.57	1.95
	Al	0.00	-0.78	2.59
	Al	1.43	2.20	-0.06
	Al	-1.43	2.20	-0.06
	Al	2.26	0.08	1.56
	Al	-2.26	0.08	1.56
	Al	0.00	1.92	-2.27
	Al	0.00	-0.64	-2.50
	Al	1.31	-2.32	0.53
	Al	-1.31	-2.32	0.53
	Al	2.40	-0.23	-1.17
	Al	-2.40	-0.23	-1.17
	C	0.00	2.09	3.87
	O	0.00	1.64	4.98
	O	0.00	3.13	3.17

Table S 9: Coordinates of $[Al_{12}Cu]-CO_2$

System	Atom type	X [Å]	Y [Å]	Z [Å]
$[Al_{12}Cu]-CO_2$	Al	0.00	0.02	-0.07
	Cu	0.00	1.74	1.51
	Al	0.00	-1.01	2.51
	Al	1.98	2.00	-0.22
	Al	-1.98	2.00	-0.22
	Al	2.21	0.13	1.58
	Al	-2.21	0.13	1.58
	Al	0.00	1.99	-2.02
	Al	0.00	-0.70	-2.55
	Al	1.37	-2.24	0.31
	Al	-1.37	-2.24	0.31
	Al	2.36	-0.41	-1.35
	Al	-2.36	-0.41	-1.35
	C	0.00	2.45	4.51
	O	0.00	1.96	5.57
	O	0.00	2.96	3.45

Table S 10: Coordinates of $[Al_{12}Zr]$

System	Atom type	X [Å]	Y [Å]	Z [Å]
$[Al_{12}Zr]$	Al	0.00	0.37	0.13
	Zr	0.00	2.54	1.86
	Al	0.00	-0.22	2.67
	Al	1.39	2.44	-0.66
	Al	-1.39	2.44	-0.66
	Al	2.24	0.79	1.40
	Al	-2.24	0.79	1.40
	Al	0.00	0.86	-2.49
	Al	0.00	-1.96	-1.73
	Al	1.38	-1.79	0.83
	Al	-1.38	-1.79	0.83
	Al	2.24	-0.16	-1.22
	Al	-2.24	-0.16	-1.22

Table S 11: Coordinates of $[Al_{12}Mn]$

System	Atom type	X [Å]	Y [Å]	Z [Å]
$[Al_{12}Mn]$	Al	-0.51	0.04	-0.02
	Mn	-0.54	1.14	2.61
	Al	-0.67	-1.48	2.40
	Al	1.18	2.16	0.90
	Al	-1.61	2.46	0.57
	Al	1.55	-0.20	1.94
	Al	-2.76	0.19	1.51
	Al	0.02	2.25	-1.51
	Al	0.54	-0.05	-2.63
	Al	1.03	-2.24	0.38
	Al	-0.54	-2.18	-1.75
	Al	2.21	0.10	-0.58
	Al	-2.18	-2.09	0.28

Table S 12: Coordinates of $[Al_{12}Fe]$

System	Atom type	X [Å]	Y [Å]	Z [Å]
$[Al_{12}Fe]$	Al	0.47	-0.13	-0.26
	Fe	-0.01	0.86	2.25
	Al	-0.12	-1.66	2.08
	Al	1.77	2.03	0.72
	Al	-1.01	2.23	0.37
	Al	2.30	-0.29	1.73
	Al	-2.00	-0.05	1.21
	Al	0.66	2.18	-1.69
	Al	0.54	-2.31	-2.02
	Al	1.71	-2.48	0.34
	Al	-1.43	-2.15	-0.28
	Al	0.02	0.00	-3.03
	Al	-2.01	0.38	-1.39

Table S 13: Coordinates of $[Al_{12}Ru]$

System	Atom type	X [Å]	Y [Å]	Z [Å]
$[Al_{12}Ru]$	Al	0.00	-0.20	0.36
	Ru	0.00	1.18	2.51
	Al	0.00	-2.70	1.50
	Al	1.38	2.18	0.69
	Al	-1.37	2.18	0.69
	Al	2.05	-0.03	2.10
	Al	-2.05	-0.03	2.10
	Al	0.00	1.90	-1.56
	Al	0.00	-0.55	-2.30
	Al	1.35	-2.42	-0.88
	Al	-1.35	-2.42	-0.88
	Al	2.52	-0.14	-0.63
	Al	-2.52	-0.14	-0.63

Table S 14: Coordinates of $[Al_{12}Co]$

System	Atom type	X [Å]	Y [Å]	Z [Å]
$[Al_{12}Co]$	Al	-0.05	-0.06	-0.18
	Co	0.15	1.93	1.62
	Al	-0.12	-0.32	2.65
	Al	1.57	2.03	-0.41
	Al	-1.01	2.79	-0.29
	Al	2.10	0.39	1.62
	Al	-2.07	0.87	1.28
	Al	-1.39	1.12	-2.26
	Al	1.11	0.39	-2.59
	Al	1.15	-2.18	0.96
	Al	-1.49	-2.03	1.13
	Al	2.57	-0.74	-0.76
	Al	-2.57	-0.77	-0.89

Table S 15: Coordinates of $[Al_{12}Ni]$

System	Atom type	X [Å]	Y [Å]	Z [Å]
$[Al_{12}Ni]$	Al	0.00	-0.13	-0.04
	Ni	0.00	1.38	1.84
	Al	0.00	-0.77	2.68
	Al	1.42	2.13	-0.04
	Al	-1.42	2.13	-0.04
	Al	2.26	0.12	1.52
	Al	-2.26	0.12	1.52
	Al	0.00	2.11	-2.26
	Al	0.00	-0.46	-2.64
	Al	1.33	-2.30	0.74
	Al	-1.33	-2.30	0.74
	Al	2.40	-0.26	-1.24
	Al	-2.40	-0.26	-1.24

Table S 16: Coordinates of $[Al_{12}Cu]$

System	Atom type	X [Å]	Y [Å]	Z [Å]
$[Al_{12}Cu]$	Al	0.00	-0.02	-0.15
	Cu	0.00	1.55	1.61
	Al	0.00	-0.93	2.49
	Al	1.92	2.01	-0.22
	Al	-1.92	2.01	-0.22
	Al	2.24	0.15	1.56
	Al	-2.24	0.15	1.56
	Al	0.00	2.02	-2.07
	Al	0.00	-0.60	-2.68
	Al	1.41	-2.22	0.41
	Al	-1.41	-2.22	0.41
	Al	2.35	-0.44	-1.34
	Al	-2.35	-0.44	-1.34

Table S 17: Coordinates of $([Al_{12}Zr]{-}CO_2)^+$

System	Atom type	X [Å]	Y [Å]	Z [Å]
$([Al_{12}Zr]{-}CO_2)^+$	Al	0.00	0.37	0.12
	Zr	0.00	2.52	1.91
	Al	0.00	-0.40	2.67
	Al	1.42	2.47	-0.70
	Al	-1.42	2.47	-0.70
	Al	2.34	0.76	1.26
	Al	-2.34	0.76	1.26
	Al	0.00	1.12	-2.53
	Al	0.00	-1.90	-1.36
	Al	1.43	-1.81	0.94
	Al	-1.43	-1.81	0.94
	Al	2.15	-0.19	-1.30
	Al	-2.15	-0.19	-1.30
	C	0.00	1.34	3.77
	O	0.00	0.26	4.46
	O	0.00	2.57	4.11

Table S 18: Coordinates of $([Al_{12}Mn]{-}CO_2)^+$

System	Atom type	X [Å]	Y [Å]	Z [Å]
$([Al_{12}Mn]{-}CO_2)^+$	Al	-0.51	0.03	0.04
	Mn	-0.45	1.10	2.57
	Al	-0.77	-1.55	2.42
	Al	1.40	2.27	0.83
	Al	-1.72	2.32	0.66
	Al	1.50	-0.28	1.92
	Al	-2.75	0.04	1.49
	Al	-0.05	2.33	-1.37
	Al	0.64	0.12	-2.56
	Al	0.80	-2.40	0.49
	Al	-0.50	-2.09	-1.75
	Al	2.28	0.15	-0.54
	Al	-2.21	-2.17	0.20
	C	0.67	2.63	2.86
	O	0.09	2.49	3.95
	O	1.57	3.40	2.36

Table S 19: Coordinates of $([Al_{12}Fe]-CO_2)^+$

System	Atom type	X [Å]	Y [Å]	Z [Å]
$([Al_{12}Fe]-CO_2)^+$	Al	0.48	-0.09	-0.21
	Fe	-0.12	0.92	2.26
	Al	-0.21	-1.62	2.16
	Al	1.70	2.07	0.72
	Al	-1.11	2.26	0.35
	Al	2.23	-0.27	1.78
	Al	-2.06	-0.03	1.19
	Al	0.58	2.23	-1.69
	Al	0.60	-2.30	-1.99
	Al	1.63	-2.49	0.46
	Al	-1.33	-2.18	-0.22
	Al	0.08	0.00	-3.05
	Al	-1.94	0.42	-1.44
	C	-0.18	3.16	4.42
	O	0.01	2.03	4.11
	O	-0.37	4.26	4.72

Table S 20: Coordinates of $([Al_{12}Ru]-CO_2)^+$

System	Atom type	X [Å]	Y [Å]	Z [Å]
$([Al_{12}Ru]-CO_2)^+$	Al	0.00	-0.17	0.23
	Ru	0.00	1.16	2.52
	Al	0.00	-2.45	1.60
	Al	1.41	2.14	0.67
	Al	-1.41	2.14	0.67
	Al	2.02	-0.14	2.11
	Al	-2.02	-0.14	2.11
	Al	0.00	1.94	-1.59
	Al	0.00	-0.48	-2.46
	Al	1.31	-2.44	-0.92
	Al	-1.31	-2.44	-0.92
	Al	2.60	-0.25	-0.54
	Al	-2.60	-0.25	-0.54
	C	0.00	3.15	3.34
	O	0.00	2.33	4.29
	O	0.00	4.29	2.99

Table S 21: Coordinates of $([Al_{12}Co]{-}CO_2)^+$

System	Atom type	X [Å]	Y [Å]	Z [Å]
$([Al_{12}Co]{-}CO_2)^+$	Al	-0.03	0.01	-0.19
	Co	0.12	1.96	1.80
	Al	-0.13	-0.43	2.79
	Al	1.54	2.20	-0.41
	Al	-0.99	2.66	-0.35
	Al	2.00	0.41	1.45
	Al	-1.99	0.83	1.28
	Al	-1.32	1.01	-2.36
	Al	1.21	0.67	-2.56
	Al	1.14	-2.20	1.11
	Al	-1.49	-2.00	1.15
	Al	2.48	-0.99	-0.91
	Al	-2.63	-0.77	-0.92
	C	0.04	1.58	3.60
	O	-0.09	0.59	4.40
	O	0.14	2.82	3.67

Table S 22: Coordinates of $([Al_{12}Ni]{-}CO_2)^+$

System	Atom type	X [Å]	Y [Å]	Z [Å]
$([Al_{12}Ni]{-}CO_2)^+$	Al	0.00	-0.25	-0.13
	Ni	0.00	1.26	1.85
	Al	0.00	-1.00	2.47
	Al	1.38	2.05	-0.06
	Al	-1.38	2.05	-0.06
	Al	2.26	-0.18	1.35
	Al	-2.26	-0.18	1.35
	Al	0.00	2.18	-2.32
	Al	0.00	-0.34	-2.80
	Al	1.32	-2.53	0.49
	Al	-1.32	-2.53	0.49
	Al	2.37	-0.17	-1.41
	Al	-2.37	-0.17	-1.41
	C	0.00	2.73	4.59
	O	0.00	2.65	5.75
	O	0.00	2.80	3.40

Table S 23: Coordinates of $([Al_{12}Cu]{-}CO_2)^+$

System	Atom type	X [Å]	Y [Å]	Z [Å]
$([Al_{12}Cu]{-}CO_2)^+$	Al	0.00	0.05	0.00
	Cu	0.00	1.91	1.44
	Al	0.00	-1.30	2.48
	Al	2.07	1.97	-0.26
	Al	-2.07	1.97	-0.27
	Al	2.16	0.19	1.65
	Al	-2.16	0.19	1.65
	Al	0.00	1.95	-2.00
	Al	0.00	-0.70	-2.42
	Al	1.48	-2.17	0.29
	Al	-1.48	-2.17	0.29
	Al	2.41	-0.40	-1.40
	Al	-2.41	-0.40	-1.40
	C	0.00	2.43	4.51
	O	0.00	2.05	5.60
	O	0.00	2.83	3.39

Table S 24: Coordinates of $[Al_{12}Zr]^+$

System	Atom type	X [Å]	Y [Å]	Z [Å]
$[Al_{12}Zr]^+$	Al	0.00	0.38	0.13
	Zr	0.00	2.51	1.83
	Al	0.00	-0.27	2.67
	Al	1.40	2.42	-0.70
	Al	-1.40	2.42	-0.70
	Al	2.27	0.76	1.38
	Al	-2.27	0.76	1.38
	Al	0.00	0.87	-2.50
	Al	0.00	-1.80	-1.60
	Al	1.39	-1.80	0.84
	Al	-1.39	-1.80	0.84
	Al	2.24	-0.15	-1.22
	Al	-2.24	-0.15	-1.22

Table S 25: Coordinates of $[Al_{12}Mn]^+$

System	Atom type	X [Å]	Y [Å]	Z [Å]
$[Al_{12}Mn]^+$	Al	-0.54	0.05	-0.03
	Mn	-0.56	1.13	2.57
	Al	-0.67	-1.51	2.47
	Al	1.22	2.21	0.93
	Al	-1.51	2.49	0.57
	Al	1.52	-0.18	1.94
	Al	-2.72	0.11	1.55
	Al	0.10	2.24	-1.52
	Al	0.55	-0.07	-2.69
	Al	0.88	-2.26	0.42
	Al	-0.54	-2.21	-1.80
	Al	2.14	0.23	-0.61
	Al	-2.12	-2.15	0.29

Table S 26: Coordinates of $[Al_{12}Fe]^+$

System	Atom type	X [Å]	Y [Å]	Z [Å]
$[Al_{12}Fe]^+$	Al	0.52	-0.12	-0.28
	Fe	-0.01	0.85	2.23
	Al	-0.14	-1.68	2.14
	Al	1.71	2.04	0.70
	Al	-1.04	2.28	0.40
	Al	2.24	-0.33	1.73
	Al	-1.98	-0.04	1.22
	Al	0.60	2.20	-1.70
	Al	0.53	-2.33	-2.07
	Al	1.66	-2.52	0.35
	Al	-1.31	-2.19	-0.22
	Al	0.01	-0.02	-3.08
	Al	-1.92	0.50	-1.40

Table S 27: Coordinates of $[Al_{12}Ru]^+$

System	Atom type	X [Å]	Y [Å]	Z [Å]
$[Al_{12}Ru]^+$	Al	0.00	-0.12	0.27
	Ru	0.00	1.23	2.48
	Al	0.00	-2.52	1.58
	Al	1.39	2.22	0.69
	Al	-1.39	2.22	0.69
	Al	1.94	-0.14	2.12
	Al	-1.95	-0.14	2.12
	Al	0.00	1.96	-1.59
	Al	0.00	-0.48	-2.44
	Al	1.30	-2.44	-0.93
	Al	-1.30	-2.44	-0.93
	Al	2.62	-0.27	-0.49
	Al	-2.62	-0.27	-0.49

Table S 28: Coordinates of $[Al_{12}Co]^+$

System	Atom type	X [Å]	Y [Å]	Z [Å]
$[Al_{12}Co]^+$	Al	0.03	-0.22	-0.11
	Co	0.17	1.89	1.64
	Al	-0.24	-0.29	2.60
	Al	1.19	2.00	-0.59
	Al	-1.00	3.30	0.08
	Al	2.11	0.46	1.52
	Al	-1.99	1.00	0.88
	Al	-1.32	1.41	-1.91
	Al	0.87	0.18	-2.70
	Al	1.35	-2.13	1.42
	Al	-1.34	-2.26	1.01
	Al	2.52	-1.04	-0.78
	Al	-2.42	-0.87	-1.18

Table S 29: Coordinates of $[Al_{12}Ni]^+$

System	Atom type	X [Å]	Y [Å]	Z [Å]
$[Al_{12}Ni]^+$	Al	0.00	-0.22	-0.03
	Ni	0.00	1.40	1.81
	Al	0.00	-0.72	2.72
	Al	1.37	2.13	-0.07
	Al	-1.37	2.13	-0.07
	Al	2.26	0.03	1.50
	Al	-2.26	0.03	1.50
	Al	0.00	2.16	-2.34
	Al	0.00	-0.38	-2.67
	Al	1.32	-2.39	0.87
	Al	-1.32	-2.39	0.87
	Al	2.38	-0.13	-1.28
	Al	-2.38	-0.13	-1.28

Table S 30: Coordinates of $[Al_{12}Cu]^+$

System	Atom type	X [Å]	Y [Å]	Z [Å]
$[Al_{12}Cu]^+$	Al	0.00	-0.37	-0.21
	Cu	0.00	2.13	0.82
	Al	0.00	-1.86	2.25
	Al	2.27	1.60	-0.14
	Al	-2.27	1.60	-0.14
	Al	1.43	0.43	2.03
	Al	-1.43	0.43	2.03
	Al	0.00	2.03	-1.65
	Al	0.00	-0.50	-2.83
	Al	2.21	-1.75	0.60
	Al	-2.21	-1.75	0.60
	Al	2.34	-0.50	-1.67
	Al	-2.34	-0.50	-1.67

Table S 31: Relaxed structures of $[Al_{12}M]$ clusters with and without adsorbed CO_2 after adiabatic ionization.

	
$([Al_{12}Zr]-CO_2)^+$	$[Al_{12}Zr]^+$
	
$([Al_{12}Mn]-CO_2)^+$	$[Al_{12}Mn]^+$
	
$([Al_{12}Fe]-CO_2)^+$	$[Al_{12}Fe]^+$
	
$([Al_{12}Ru]-CO_2)^+$	$[Al_{12}Ru]^+$
	
$([Al_{12}Co]-CO_2)^+$	$[Al_{12}Co]^+$
	
$([Al_{12}Ni]-CO_2)^+$	$[Al_{12}Ni]^+$
	
$([Al_{12}Cu]-CO_2)^+$	$[Al_{12}Cu]^+$

peak in the Al pDOS (Figure S1) at 1 eV compared to $[Al_{12}Zr]-CO_2$ and $[Al_{12}Mn]-CO_2$. Especially in the case of $[Al_{12}Ru]-CO_2$, there is a lot of high-intensity peaks very close to the Fermi-energy at about -1 eV in the Al projected DOS. $[Al_{12}Zr]-CO_2$ has a peak below the Fermi-energy that is even higher in intensity but it is located at a lower energy. $[Al_{12}Mn]-CO_2$ exhibits peaks with much lower intensity in these regions which could explain its small LICT values. Comparison of the Fe and the Cu doped clusters yields very similar results among both systems for the Al projected DOS. A possible reason for the earlier onset of LICT in the Fe doped cluster could be the multiple small peaks located around the Fermi-energy in the transition-metal projected DOS (Figure S2). The Cu doped system with its high intensity peak at -2.5 eV in the transition-metal projected DOS results in a smaller and sharper energy window in which LICT can be observed while the small, evenly spread transition-metal states of the Fe cluster result in a more even distribution of LICT excitations.

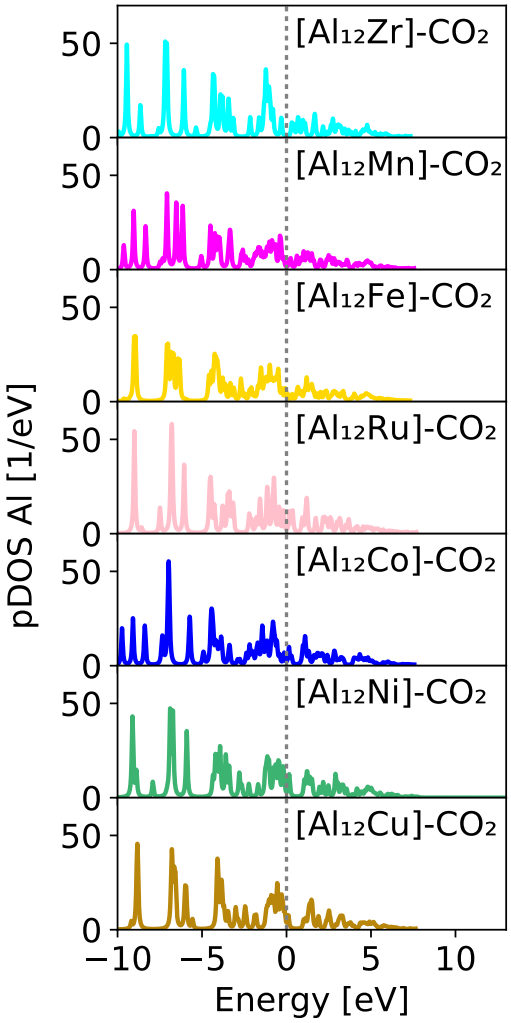

Figure S 1: DOS projected onto Al atomic orbitals for transition-metal doped aluminium clusters with adsorbed CO_2. The zero of energy is set to the Fermi-level and denoted by a grey vertical line. A broadening of 0.05 eV has been used.

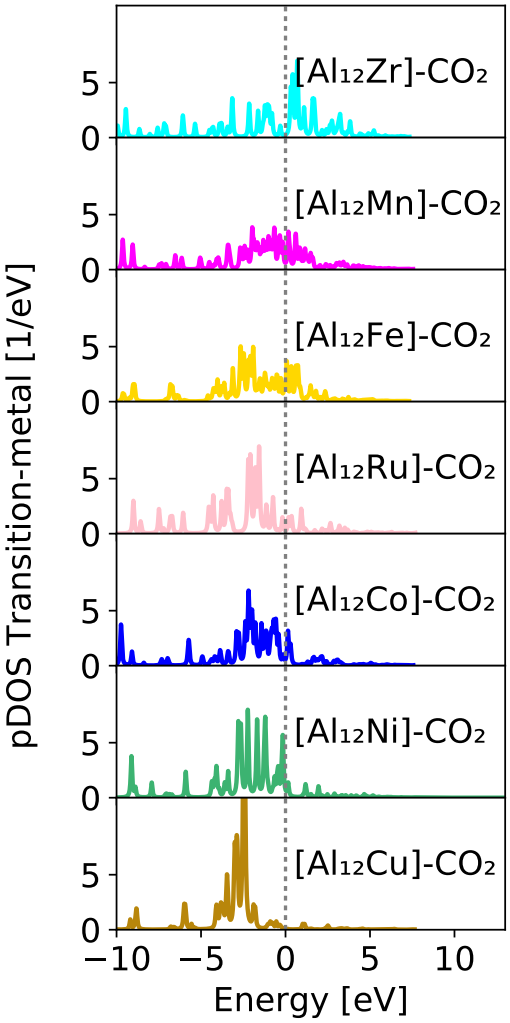

Figure S 2: DOS projected onto the atomic orbitals of the transition-metal for transition-metal doped aluminium clusters with adsorbed CO_2. The zero of energy is set to the Fermi-level and denoted by a grey vertical line. A broadening of 0.05 eV has been used.