Supporting Information

for

A new class of hybrid materials for detection, capture, and "on-demand" release of carbon monoxide

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Synthesis of the materials

Carbon monoxide cylinder was purchased from BOC. Anhydrous quality of THF, diethyl ether and methanol were purchased from Sigma-Aldrich. *o*-carborane was purchased from Katchem and used as received. Sylgard 184 PDMS gel kit was purchased from Dow Corning. All other regents were obtained from commercial suppliers and used as received. The preparation of complexes [Os(*p*-cym)(1,2-dicarba-*closo*-dodecaborane-1,2-dithiolato)] (**1**) and [Ir(η^5-pentamethylcyclopentadienyl)(1,2-dicarba-*closo*-dodecarborane-1,2-dithiolato)] (**2**) was based on previous reports.[1-2] All gels were prepared using 1.7 g of PDMS to 0.17 g of crosslinker, with the required amount of complex mixed in. The gel was placed on a "winged" glass microscope slide structure and heated at 523 K using a Master Proheat Varitemp Heatgun for 3 – 4 minutes or until solidified and a complex melting effect is observed. The gels were left to cool and stored under nitrogen.

Instrumentation

UV-visible absorption spectra were recorded using a Varian CARY 50 Bio UV-Visible spectrophotometer at 298 K using 1 cm path length quartz cuvettes. All infra-red spectra were recorded on a Bruker Alpha Platinum ATR. Scanning electron microscopy micrographs were obtained on a Jeol 4500 FIB/SEM.

Methods

Geometry optimizations were carried out using the M11-L DFT functional[3] coupled with the SDD basis set[4] for the metal ions and the def2-TZVP basis set[5] for the lighter elements. The singlet, triplet and quintet spin states were considered for all the models. Vibrational frequencies were calculated to ensure the absence of imaginary frequencies and to obtain the IR spectra. UV-vis spectra were computed using the time dependent density functional theory (TD-DFT) method on the optimized structures using the same DFT functionals and basis sets. All calculations were performed in vacuum and in THF by employing the CPCM solvation model field.[6] In addition, calculations were also carried out using the B3LYP, PBE0 and TPSSh DFT functionals providing qualitatively very similar results. All calculations were performed by utilizing the Gaussian 09 software package.[7]

Calculations data

Table S1. Zero point corrected electronic energies (a.u.) and relative energies (kcal/mol) for 1, [1-CO], 2 and [2-CO] computed by M-11L/def2-TZVP in vacuum.

Structure	E W ZPC	E rel
1_sm1_m11l_tz	-1607.572478	0.00
1_sm3_m11l_tz	-1607.526884	28.61
1_sm5_m11l_tz	-1607.474258	61.63
[1-CO]_sm1_m11l_tz	-1720.920418	0.00
[1-CO]_sm3_m11l_tz	-1720.861564	36.93

[1-CO]_sm5_m11l_tz	-1720.832680	55.06
2_sm1_m11l_tz	-1425.358141	0.00
2_sm3_m11l_tz	-1425.325391	20.55
2_sm5_m11l_tz	-1425.244084	71.57
[2-CO]_sm1_m11l_tz	-1538.705984	0.00
[2-CO]_sm3_m11l_tz	-1538.642249	39.99
[2-CO]_sm5_m11l_tz	-1538.591559	71.80

Table S2. Zero point corrected electronic energies (a.u.) and relative energies (kcal/mol) for 1, [1-CO], 2 and [2-CO] computed by B3LYP/def2-TZVP in vacuum.

Structure	E W ZPC	E rel
1_sm1_b3lyp_tz	-1607.498721	0.00
1_sm3_b3lyp_tz	-1607.441671	35.80
1_sm5_b3lyp_tz	-1607.406108	58.12
[1-CO]_sm1_b3lyp_tz	-1720.878876	0.00
[1-CO]_sm3_b3lyp_tz	-1720.821894	35.76
[1-CO]_sm5_b3lyp_tz	-1720.799425	49.86
2_sm1_b3lyp_tz	-1425.242930	0.00
2_sm3_b3lyp_tz	-1425.213178	18.67
2_sm5_b3lyp_tz	-1425.129807	70.99
[2-CO]_sm1_b3lyp_tz	-1538.623498	0.00
[2-CO]_sm3_b3lyp_tz	-1538.581988	26.05

[2-CO]_sm5_b3lyp_tz	-1538.517357	66.60

Table S3. Zero point corrected electronic energies (a.u.) and relative energies (kcal/mol) for 1, [1-CO], 2 and [2-CO] computed by PBE0/def2-TZVP in vacuum.

Structure	E W ZPC	E rel
1_sm1_pbe0_tz	-1606.294754	0.00
1_sm3_pbe0_tz	-1606.248533	29.00
1_sm5_pbe0_tz	-1606.190712	65.29
[1-CO]_sm1_pbe0_tz	-1719.550883	0.00
[1-CO]_sm3_pbe0_tz	-1719.486610	40.33
[1-CO]_sm5_pbe0_tz	-1719.443155	67.60
2_sm1_pbe0_tz	-1424.277194	0.00
2_sm3_pbe0_tz	-1424.242858	21.55
2_sm5_pbe0_tz	-1424.152130	78.48
[2-CO]_sm1_pbe0_tz	-1537.534688	0.00
[2-CO]_sm3_pbe0_tz	-1537.480010	34.31
[2-CO]_sm5_pbe0_tz	-1537.412964	76.38

Table S4. Zero point corrected electronic energies (a.u.) and relative energies (kcal/mol) for 1, [1-CO], 2 and [2-CO] computed by TPSSh/def2-TZVP in vacuum.

Structure	E W ZPC	E rel
1_sm1_tpssh_tz	-1607.620499	0.00
1_sm3_tpssh_tz	-1607.574069	29.14
1_sm5_tpssh_tz	-1607.514214	66.69
[1-CO]_sm1_tpssh_tz	-1721.002690	0.00

[1-CO]_sm3_tpssh_tz	-1720.942026	38.07
[1-CO]_sm5_tpssh_tz	-1720.897784	65.83
2_sm1_tpssh_tz	-1425.339112	0.00
2_sm3_tpssh_tz	-1425.304293	21.85
2_sm5_tpssh_tz	-1425.214865	77.97
[2-CO]_sm1_tpssh_tz	-1538.722281	0.00
[2-CO]_sm3_tpssh_tz	-1538.656167	41.49
[2-CO]_sm5_tpssh_tz	-1538.604552	73.88

Table S5. Zero point corrected electronic energies (a.u.) and relative energies (kcal/mol) for 1, [1-CO], 2 and [2-CO] computed by M-11L/def2-TZVP in THF.

Structure	E W ZPC	E rel
1_sm1_m11l_tz_thf	-1607.5861210	0.00
1_sm3_m11l_tz_thf	-1607.5395510	29.22
1_sm5_m11l_tz_thf	-1607.4956390	56.78
[1-CO]_sm1_m11l_tz_thf	-1720.9381670	0.00
[1-CO]_sm3_m11l_tz_thf	-1720.8722280	41.38
[1-CO]_sm5_m11l_tz_thf	-1720.8434410	59.44
2_sm1_m11l_tz_thf	-1425.3725290	0.00
2_sm3_m11l_tz_thf	-1425.3339500	24.21
2_sm5_m11l_tz_thf	-1425.2669450	66.26
[2-CO]_sm1_m11l_tz_thf	-1538.7195190	0.00
[2-CO]_sm3_m11l_tz_thf	-1538.6518760	42.45
[2-CO]_sm5_m11l_tz_thf	-1538.6032610	72.95

Table S6. Zero point corrected electronic energies (a.u.) and relative energies (kcal/mol) for **1**, **[1-CO]**, **2** and **[2-CO]** computed by B3LYP/def2-TZVP in THF.

Structure	E W ZPC	E rel
1_sm1_b3lyp_tz_thf	-1607.5125990	0.00
1_sm3_b3lyp_tz_thf	-1607.4725100	25.16
1_sm5_b3lyp_tz_thf	-1607.4272510	53.56
[1-CO]_sm1_b3lyp_tz_thf	-1720.8975600	0.00
[1-CO]_sm3_b3lyp_tz_thf	-1720.8338380	39.99

[1-CO]_sm5_b3lyp_tz_thf	-1720.8147420	51.97
2_sm1_b3lyp_tz_thf	-1425.2572570	0.00
2_sm3_b3lyp_tz_thf	-1425.2216060	22.37
2_sm5_b3lyp_tz_thf	-1425.1488590	68.02
[2-CO]_sm1_b3lyp_tz_thf	-1538.6377260	0.00
[2-CO]_sm3_b3lyp_tz_thf	-1538.5905660	29.59
[2-CO]_sm5_b3lyp_tz_thf	-1538.5290170	68.22

Table S7. Zero point corrected electronic energies (a.u.) and relative energies (kcal/mol) for 1, [1-CO], 2 and [2-CO] computed by PBE0/def2-TZVP in THF.

Structure	E W ZPC	E rel
1_sm1_pbe0_tz_thf	-1606.3087100	0.00
1_sm3_pbe0_tz_thf	-1606.2619550	29.34
1_sm5_pbe0_tz_thf	-1606.2089550	62.60
[1-CO]_sm1_pbe0_tz_thf	-1719.5692030	0.00
[1-CO]_sm3_pbe0_tz_thf	-1719.4985190	44.35
[1-CO]_sm5_pbe0_tz_thf	-1719.4541850	72.17
2_sm1_pbe0_tz_thf	-1424.2917320	0.00
2_sm3_pbe0_tz_thf	-1424.2512830	25.38
2_sm5_pbe0_tz_thf	-1424.1702640	76.22
[2-CO]_sm1_pbe0_tz_thf	-1537.5490030	0.00
[2-CO]_sm3_pbe0_tz_thf	-1537.4882610	38.12
[2-CO]_sm5_pbe0_tz_thf	-1537.4232430	78.92

Table S8. Zero point corrected electronic energies (a.u.) and relative energies (kcal/mol) for 1, [1-CO], 2 and [2-CO] computed by TPSSh/def2-TZVP in THF.

Structure	E W ZPC	E rel
1_sm1_tpssh_tz_thf	-1607.6338390	0.00
1_sm3_tpssh_tz_thf	-1607.5866240	29.63
1_sm5_tpssh_tz_thf	-1607.5311950	64.41
[1-CO]_sm1_tpssh_tz_thf	-1721.0206010	0.00
[1-CO]_sm3_tpssh_tz_thf	-1720.9534200	42.16
[1-CO]_sm5_tpssh_tz_thf	-1720.9079520	70.69
2_sm1_tpssh_tz_thf	-1425.3530630	0.00
2_sm3_tpssh_tz_thf	-1425.3126100	25.38
2_sm5_tpssh_tz_thf	-1425.2323510	75.75
[2-CO]_sm1_tpssh_tz_thf	-1538.7364780	0.00
[2-CO]_sm3_tpssh_tz_thf	-1538.6661210	44.15
[2-CO]_sm5_tpssh_tz_thf	-1538.6144930	76.55

Table S9. Zero point corrected electronic energies (a.u.) and relative energies (kcal/mol) for 1, [1-CO], 2 and [2-CO] encapsulated by HMDSO computed by M-11L/def2-TZVP in Vacuum.

Structure	E W ZPC	E rel
1_encap_sm1_m11l_vac	-2501.87510713	0.0
1_encap_sm3_m11l_vac	-2501.82654958	30.5
1_encap_sm5_m11l_vac	-2501.78055522	59.3
[1-CO]_encap_cis_sm1_m11l_vac	-2615.20762276	0.0
[1-CO]_encap_cis_sm3_m11l_vac	-2615.16241592	28.4
[1-CO]_encap_cis_sm5_m11l_vac	-2615.14212871	41.1
[1-CO]_encap_trans_sm1_m11l_vac	-2615.19802806	0.0
[1-CO]_encap_trans_sm3_m11l_vac	-2615.15993336	23.9
[1-CO]_encap_trans_sm5_m11l_vac	-2615.11659919	51.1
2_encap_sm1_m11l_vac	-2319.53335242	0.0
2_encap_sm3_m11l_vac	-2319.49758053	22.4
2_encap_sm5_m11l_vac	-2319.41572114	73.8
[2-CO]_encap_cis_sm1_m11l_vac	-2432.88626826	0.0
[2-CO]_encap_cis_sm3_m11l_vac	-2432.83623478	31.4
[2-CO]_encap_cis_sm5_m11l_vac	-2432.77157421	72.0
[2-CO]_encap_trans_sm1_m11l_vac	-2432.86642276	0.0
[2-CO]_encap_trans_sm3_m11l_vac	-2432.82488824	26.1
[2-CO]_encap_trans_sm5_m11l_vac	-2432.77219698	59.1

Table S10. Zero point corrected electronic energies (a.u.) and relative energies (kcal/mol) for 1, [1-CO], 2 and [2-CO] encapsulated by HMDSO computed by B3LYP/def2-TZVP in Vacuum.

Structure	E W ZPC	E rel
1_encap_sm1_b3lyp_vac	-2501.93475320	0.0
1_encap_sm3_b3lyp_vac	-2501.89183816	26.9
1_encap_sm5_b3lyp_vac	-2501.84314945	57.5
[1-CO]_encap_cis_sm1_b3lyp_vac	-2615.32789440	0.0
[1-CO]_encap_cis_sm3_b3lyp_vac	-2615.28638025	26.1
[1-CO]_encap_cis_sm5_b3lyp_vac	-2615.23806878	56.4
[1-CO]_encap_trans_sm1_b3lyp_vac	-2615.31105465	0.0
[1-CO]_encap_trans_sm3_b3lyp_vac	-2615.25423467	35.7
[1-CO]_encap_trans_sm5_b3lyp_vac	-2615.24293386	42.7
2_encap_sm1_b3lyp_vac	-2319.55133424	0.0
2_encap_sm3_b3lyp_vac	-2319.51977210	19.8
2_encap_sm5_b3lyp_vac	-2319.43357794	73.9
[2-CO]_encap_cis_sm1_b3lyp_vac	-2432.93887636	0.0
[2-CO]_encap_cis_sm3_b3lyp_vac	-2432.86341577	47.4
[2-CO]_encap_cis_sm5_b3lyp_vac	-2432.82845892	69.3
[2-CO]_encap_trans_sm1_b3lyp_vac	-2432.91424317	0.0
[2-CO]_encap_trans_sm3_b3lyp_vac	-2432.87366477	25.5
[2-CO]_encap_trans_sm5_b3lyp_vac	-2432.82815535	54.0

Table S11. Zero point corrected electronic energies (a.u.) and relative energies (kcal/mol) for 1, [1-CO], 2 and [2-CO] encapsulated by HMDSO computed by PBE0/def2-TZVP in Vacuum.

Structure	E W ZPC	E rel
1_encap_sm1_pbe0_vac	-2500.05117016	0.0
1_encap_sm3_pbe0_vac	-2500.00157904	31.1
1_encap_sm5_pbe0_vac	-2499.94230019	68.3
[1-CO]_encap_cis_sm1_pbe0_vac	-2613.31919292	0.0
[1-CO]_encap_cis_sm3_pbe0_vac	-2613.21519129	65.3
[1-CO]_encap_cis_sm5_pbe0_vac	-2613.20705936	70.4
[1-CO]_encap_trans_sm1_pbe0_vac	-2613.28831400	0.0
[1-CO]_encap_trans_sm3_pbe0_vac	-2613.23393891	34.1
[1-CO]_encap_trans_sm5_pbe0_vac	-2613.21150705	48.2
2_encap_sm1_pbe0_vac	-2317.90625957	0.0
2_encap_sm3_pbe0_vac	-2317.86909414	23.3
2_encap_sm5_pbe0_vac	-2317.77370300	83.2
[2-CO]_encap_cis_sm1_pbe0_vac	-2431.17114372	0.0
[2-CO]_encap_cis_sm3_pbe0_vac	-2431.09696147	46.6
[2-CO]_encap_cis_sm5_pbe0_vac	-2431.04289905	80.5
[2-CO]_encap_trans_sm1_pbe0_vac	-2431.16937512	0.0
[2-CO]_encap_trans_sm3_pbe0_vac	-2431.09721987	45.3
[2-CO]_encap_trans_sm5_pbe0_vac	-2431.04405157	78.6

Table S12. Zero point corrected electronic energies (a.u.) and relative energies (kcal/mol) for 1, [1-CO], 2 and [2-CO] encapsulated by HMDSO computed by TPSSh/def2-TZVP in Vacuum.

Structure	E W ZPC	E rel
1_encap_sm1_tpssh_vac	-2502.08940028	0.0
1_encap_sm3_tpssh_vac	-2502.00766585	51.3
1_encap_sm5_tpssh_vac	-2501.94829402	88.5
[1-CO]_encap_cis_sm1_tpssh_vac	-2615.46421530	0.0
[1-CO]_encap_cis_sm3_tpssh_vac	-2615.40798746	35.3
[1-CO]_encap_cis_sm5_tpssh_vac	-2615.34060640	77.6
[1-CO]_encap_trans_sm1_tpssh_vac	-2615.44102137	0.0
[1-CO]_encap_trans_sm3_tpssh_vac	-2615.38588059	34.6
[1-CO]_encap_trans_sm5_tpssh_vac	-2615.34539568	60.0
2_encap_sm1_tpssh_vac	-2319.61371491	0.0
2_encap_sm3_tpssh_vac	-2319.55124879	39.2
2_encap_sm5_tpssh_vac	-2319.51927753	59.3
[2-CO]_encap_cis_sm1_tpssh_vac	-2433.04348541	0.0
[2-CO]_encap_cis_sm3_tpssh_vac	-2432.96922813	46.6
[2-CO]_encap_cis_sm5_tpssh_vac	-2432.91367518	81.5
[2-CO]_encap_trans_sm1_tpssh_vac	-2433.03898521	0.0
[2-CO]_encap_trans_sm3_tpssh_vac	-2432.96973461	43.5
[2-CO]_encap_trans_sm5_tpssh_vac	-2432.91912337	75.2

Table S13. Zero point corrected electronic energies (a.u.) and relative energies (kcal/mol) for 1, [1-CO], 2 and [2-CO] encapsulated by HMDSO computed by M-11L/def2-TZVP in THF.

Structure	E W ZPC	E rel
1_encap_sm1_m11l_thf	-2501.88808184	0.0
1_encap_sm3_m11l_thf	-2501.83900252	30.8
1_encap_sm5_m11l_thf	-2501.79520405	58.3
[1-CO]_encap_cis_sm1_m11l_thf	-2615.25038358	0.0
[1-CO]_encap_cis_sm3_m11l_thf	-2615.21733493	20.7
[1-CO]_encap_cis_sm5_m11l_thf	-2615.15522972	59.7
[1-CO]_encap_trans_sm1_m11l_thf	-2615.21296746	0.0
[1-CO]_encap_trans_sm3_m11l_thf	-2615.17219162	25.6
[1-CO]_encap_trans_sm5_m11l_thf	-2615.13143100	51.2
2_encap_sm1_m11l_thf	-2319.54654626	0.0
2_encap_sm3_m11l_thf	-2319.50674528	25.0
2_encap_sm5_m11l_thf	-2319.44039452	66.6
[2-CO]_encap_cis_sm1_m11l_thf	-2432.89893122	0.0
[2-CO]_encap_cis_sm3_m11l_thf	-2432.84719476	32.5
[2-CO]_encap_cis_sm5_m11l_thf	-2432.78446252	71.8
[2-CO]_encap_trans_sm1_m11l_thf	-2432.87961610	0.0
[2-CO]_encap_trans_sm3_m11l_thf	-2432.83383489	28.7
[2-CO]_encap_trans_sm5_m11l_thf	-2432.77407591	66.2

Table S14. Zero point corrected electronic energies (a.u.) and relative energies (kcal/mol) for 1, [1-CO], 2 and [2-CO] encapsulated by HMDSO computed by B3LYP/def2-TZVP in THF.

Structure	E W ZPC	E rel
1_encap_sm1_b3lyp_thf	-2501.94900624	0.0
1_encap_sm3_b3lyp_thf	-2501.90530346	27.4
1_encap_sm5_b3lyp_thf	-2501.86613434	52.0
[1-CO]_encap_cis_sm1_b3lyp_thf	-2615.34698956	0.0
[1-CO]_encap_cis_sm3_b3lyp_thf	-2615.31382216	20.8
[1-CO]_encap_cis_sm5_b3lyp_thf	-2615.25548071	57.4
[1-CO]_encap_trans_sm1_b3lyp_thf	-2615.33077956	0.0
[1-CO]_encap_trans_sm3_b3lyp_thf	-2615.26742242	39.8
[1-CO]_encap_trans_sm5_b3lyp_thf	-2615.25487432	47.6
2_encap_sm1_b3lyp_thf	-2319.56596644	0.0
2_encap_sm3_b3lyp_thf	-2319.52925939	23.0
2_encap_sm5_b3lyp_thf	-2319.45525870	69.5
[2-CO]_encap_cis_sm1_b3lyp_thf	-2432.95493427	0.0
[2-CO]_encap_cis_sm3_b3lyp_thf	-2432.90502076	31.3
[2-CO]_encap_cis_sm5_b3lyp_thf	-2432.84154024	71.2
[2-CO]_encap_trans_sm1_b3lyp_thf	-2432.92802836	0.0
[2-CO]_encap_trans_sm3_b3lyp_thf	-2432.88428948	27.4
[2-CO]_encap_trans_sm5_b3lyp_thf	-2432.84130076	54.4

Table S15. Zero point corrected electronic energies (a.u.) and relative energies (kcal/mol) for 1, [1-CO], 2 and [2-CO] encapsulated by HMDSO computed by PBE0/def2-TZVP in THF.

Structure	E W ZPC	E rel
1_encap_sm1_pbe0_thf	-2500.06508651	0.0
1_encap_sm3_pbe0_thf	-2500.01491125	31.5
1_encap_sm5_pbe0_thf	-2499.96592266	62.2
[1-CO]_encap_cis_sm1_pbe0_thf	-2613.33813495	0.0
[1-CO]_encap_cis_sm3_pbe0_thf	-2613.28745189	31.8
[1-CO]_encap_cis_sm5_pbe0_thf	-2613.22137066	73.3
[1-CO]_encap_trans_sm1_pbe0_thf	-2613.29695389	0.0
[1-CO]_encap_trans_sm3_pbe0_thf	-2613.24617053	31.9
[1-CO]_encap_trans_sm5_pbe0_thf	-2613.22225549	46.9
2_encap_sm1_pbe0_thf	-2317.92054695	0.0
2_encap_sm3_pbe0_thf	-2317.86471461	35.0
2_encap_sm5_pbe0_thf	-2317.79519618	78.7
[2-CO]_encap_cis_sm1_pbe0_thf	-2431.18512325	0.0
[2-CO]_encap_cis_sm3_pbe0_thf	-2431.10736369	48.8
[2-CO]_encap_cis_sm5_pbe0_thf	-2431.05519481	81.5
[2-CO]_encap_trans_sm1_pbe0_thf	-2431.11519351	0.0
[2-CO]_encap_trans_sm3_pbe0_thf	-2431.09750392	11.1
[2-CO]_encap_trans_sm5_pbe0_thf	-2431.05472665	37.9

Table S16. Zero point corrected electronic energies (a.u.) and relative energies (kcal/mol) for 1, [1-CO], 2 and [2-CO] encapsulated by HMDSO computed by TPSSh/def2-TZVP in THF.

Structure	E W ZPC	E rel
1_encap_sm1_tpssh_thf	-2502.05548454	0.0
1_encap_sm3_tpssh_thf	-2502.02028143	22.1
1_encap_sm5_tpssh_thf	-2501.96790091	55.0
[1-CO]_encap_cis_sm1_tpssh_thf	-2615.47215321	0.0
[1-CO]_encap_cis_sm3_tpssh_thf	-2615.41802045	34.0
[1-CO]_encap_cis_sm5_tpssh_thf	-2615.35393368	74.2
[1-CO]_encap_trans_sm1_tpssh_thf	-2615.45012458	0.0
[1-CO]_encap_trans_sm3_tpssh_thf	-2615.39773307	32.9
[1-CO]_encap_trans_sm5_tpssh_thf	-2615.35493376	59.7
2_encap_sm1_tpssh_thf	-2319.69542133	0.0
2_encap_sm3_tpssh_thf	-2319.62114989	46.6
2_encap_sm5_tpssh_thf	-2319.53906142	98.1
[2-CO]_encap_cis_sm1_tpssh_thf	-2433.03458123	0.0
[2-CO]_encap_cis_sm3_tpssh_thf	-2432.98056950	33.9
[2-CO]_encap_cis_sm5_tpssh_thf	-2432.92239988	70.4
[2-CO]_encap_trans_sm1_tpssh_thf	-2433.01248699	0.0
[2-CO]_encap_trans_sm3_tpssh_thf	-2432.98020111	20.3
[2-CO]_encap_trans_sm5_tpssh_thf	-2432.92796578	53.0

Table S17. The thermochemistry of the CO addition.

in Vacuum	Sum of electronic and thermal enthalpies	E CO addition Kcal/mol	**in THF**	sum of electronic and thermal enthalpies	E CO addition Kcal/mol
CO_m11l_vac	-113.321128		CO_m11l_thf	-113.321697	
1_sm1_m11l_vac	-1607.548533		**1**_sm1_m11l_thf	-1607.562164	
[1-CO]_sm1_m11l_vac	-1720.894173	-15.4	**[1-CO]**_sm1_m11l_thf	-1720.911892	-17.6
2_sm1_m11l_vac	-1425.340901		**2**_sm1_m11l_thf	-1425.355250	
[2-CO]_sm1_m11l_vac	-1538.686387	-15.3	**[2-CO]**_sm1_m11l_thf	-1538.699938	-14.4

Figures S1-S3

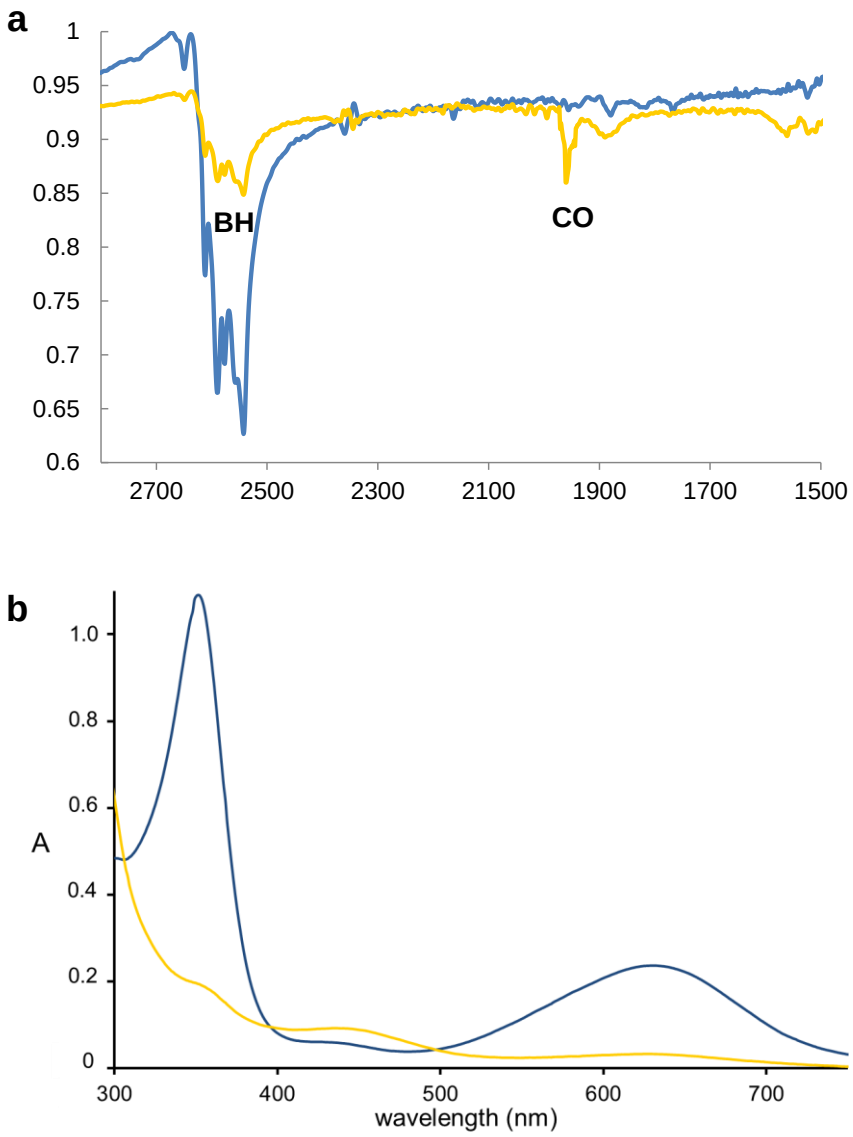

Fig. S1. a, Infrared absorption spectra of 2 and [2-CO] (recorded as solid; 2 blue line, [2-CO] yellow line). b, UV-visible absorption spectra of complexes 1 and [1-CO] (10^{-5} M, dichloromethane; 1 blue line, [1-CO] yellow line).

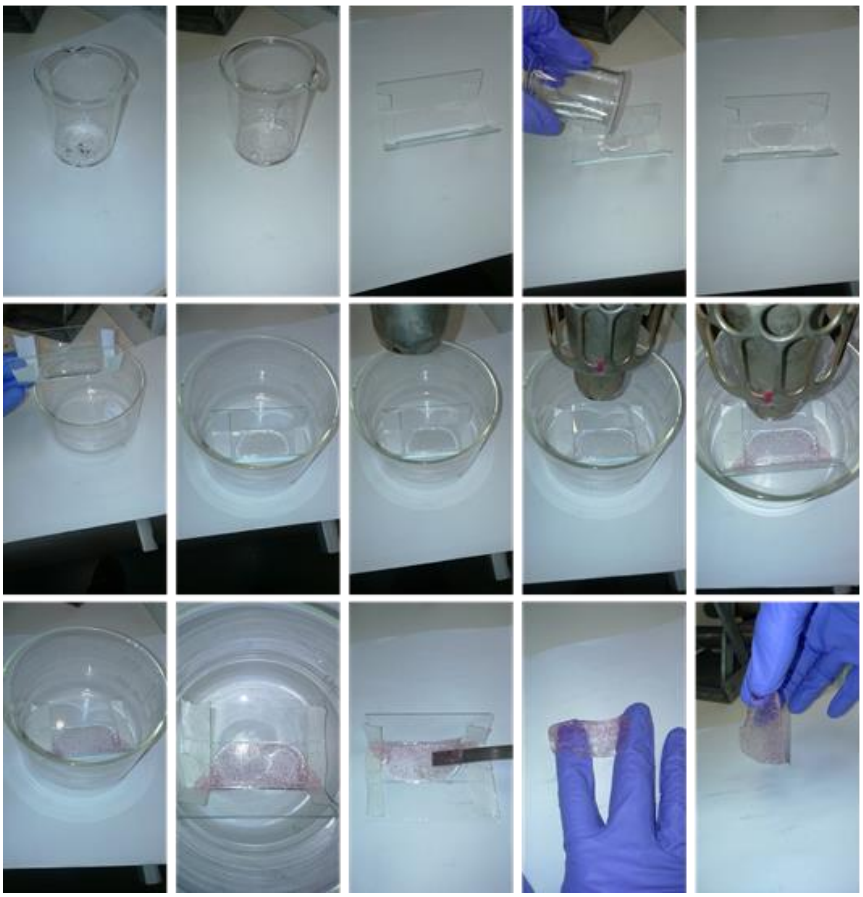

Fig. S2. Step-by-step fabrication of the hybrid silicone-based material (total time < 5 min).

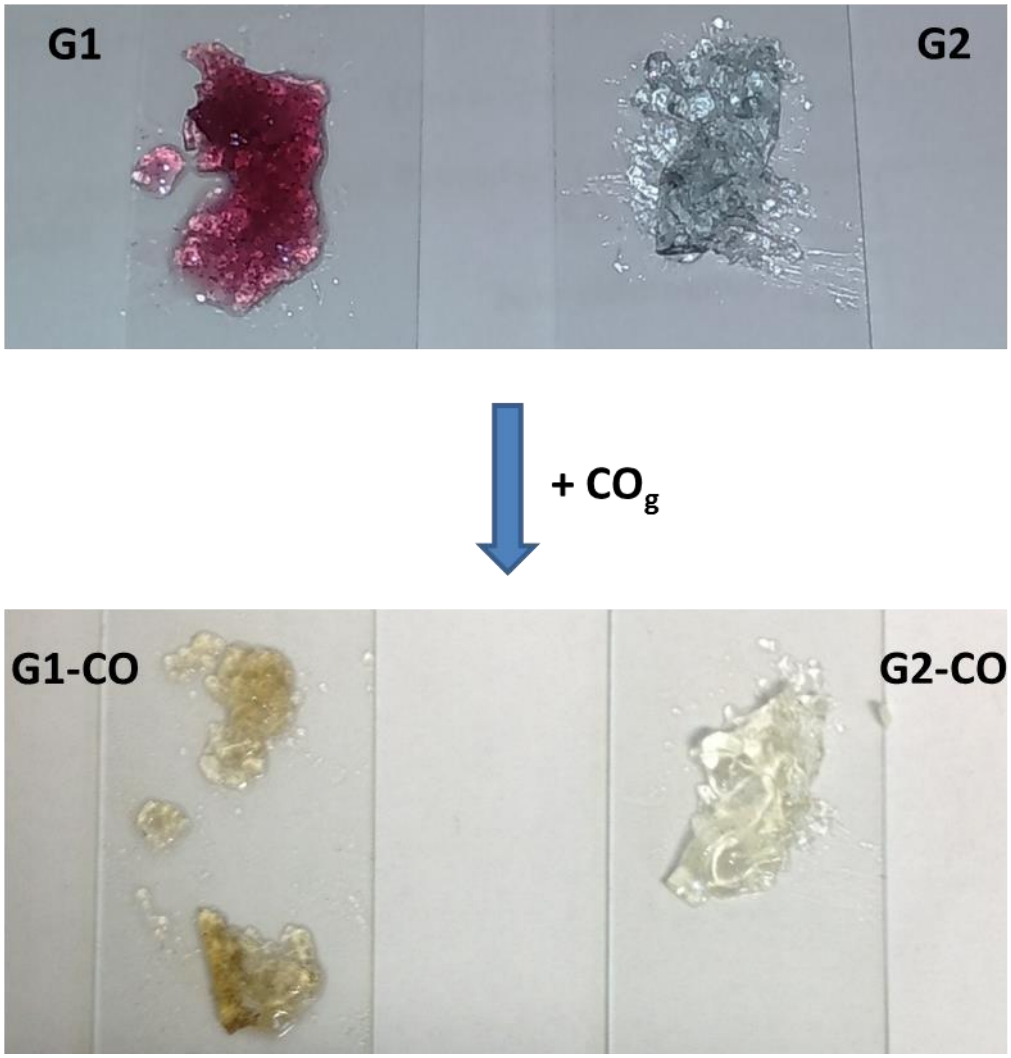

Fig. S3. Color changes of the Os and Ir gels G1 and G2 after exposure to 1 atmosphere of carbon monoxide.

Videos S1-S2

Video S1. CO-release and recycling methodology for the gel materials.

Video S2. Utilization of a gel G1-CO to perform the carbonylation reaction of 2 to [2-CO].

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