Support information

Computational Study on Tunability of Woven Covalent Organic Framework for Photocatalysis

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Table S1 Optimized structural data for complex $Cu(PDB)_2$.

	Distance/Å[a]	Distance/Å (This study)
N(1)-Cu(1)	2.06	2.10
N(2)-Cu(1)	2.06	2.07
N(3)-Cu(1)	2.10	2.11
N(4)-Cu(1)	2.03	2.04
	Angles/°[a]	Angles/°
N(4)-Cu(1)-N(1)	142.26	142.03
N(4)-Cu(1)-N(2)	126.80	125.50
N(1)-Cu(1)-N(2)	82.22	83.12
N(4)-Cu(1)-N(3)	81.55	81.63
N(1)-Cu(1)-N(3)	123.16	123.20
N(2)-Cu(1)-N(3)	95.82	96.10

[a]Reference 1.

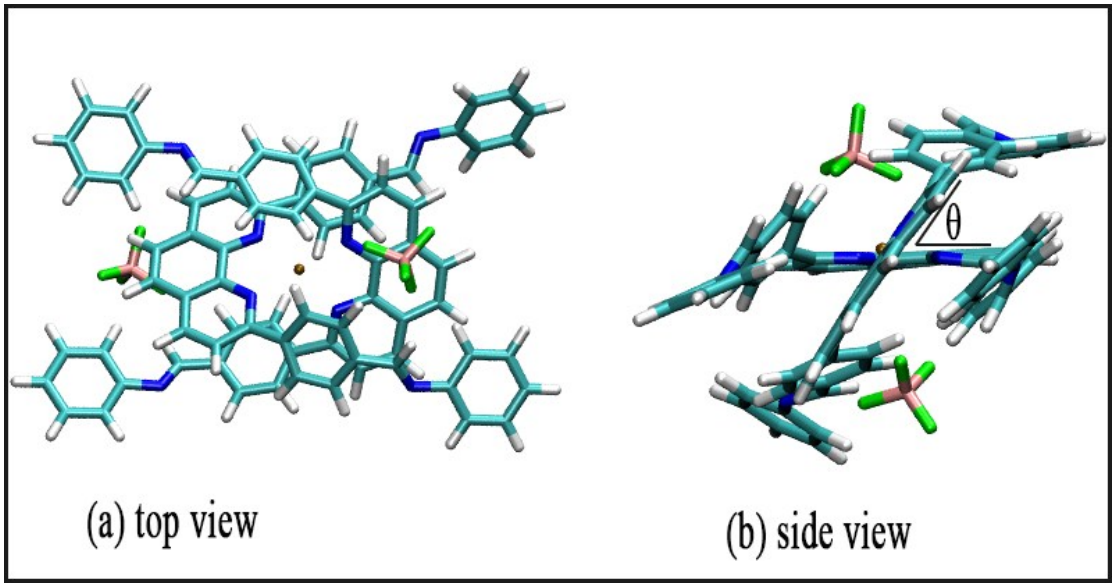

Fig. S1 Schematic structures of the cleaved fragment for Pd(II)_complex (a) top view

(b) side view.

Table S2 Optimized structural data for Pd(II)_complex.

	Distance/Å[b]	Distance/Å (This study)
N(1)-Pd(1)	2.04	2.06
N(2)-Pd(1)	2.05	2.11
N(3)-Pd(1)	2.06	2.11
N(4)-Pd(1)	2.04	2.06
	Angles/°[b]	Angles/°
N(1)-Pd(1)-N(2)	80.70	79.69
N(1)-Pd(1)-N(3)	100.50	107.64
N(1)-Pd(1)-N(4)	168.70	154.99
N(2)-Pd(1)-N(3)	163.90	146.31
N(2)-Pd(1)-N(4)	101.10	107.71
N(3)-Pd(1)-N(4)	80.90	79.78

[b]Reference 2.

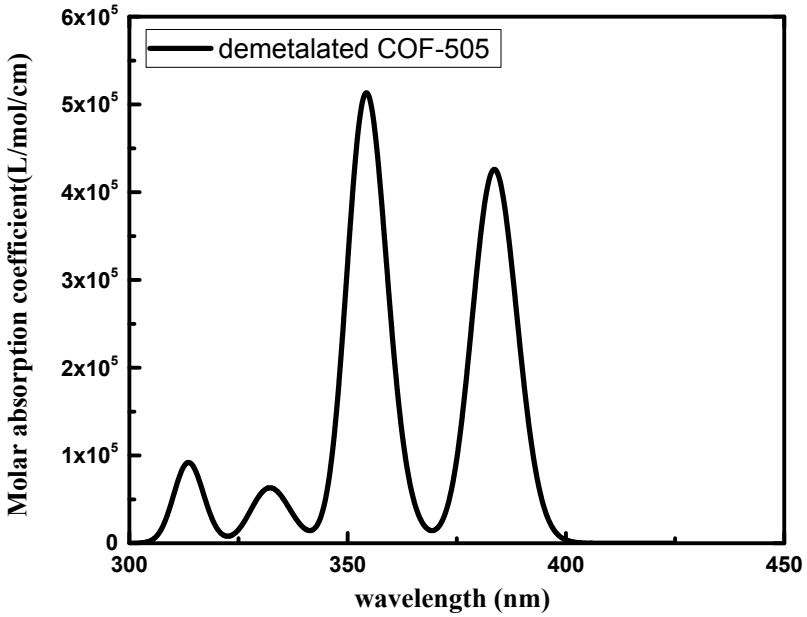

Fig. S2 Calculated UV-Vis absorption spectra of demetalated COF-505. The calculated spectra broadened by Gaussian function with an fwhm of 0.1eV.

Table S3 The contribution of metal ions with different dihedral angle to frontier molecular orbital composition (%) (The atom composition is listed in the parenthesis, the composition less than 5% is ignored)

Orbital	type	Contribution (%)	type	Contribution	type	contribution
		Cu(I) θ=49º		Cu(I) θ=59º		Cu(I)θ=69º
H-7	d+π	$16d_{x2y2}$+$44d_{z2}$(62)	π		π	
H-6	d+π	$65d_{yz}$(65)	π		π	
H-5	d+π	$73d_{xz}$(73)	d+π	$71d_{yz}$(73)	π	
H-4	π		d+π	$17d_{xy}$(18)	π	
H-3	π		π		d+π	$44d_{xz}$+$11d_{yz}$(68)
H-2	π		π		d+π	$9d_{x2y2}$+$3d_{xy}$(13)
H-1	π		π		d+π	$17d_{x2y2}$+$14d_{xy}$(34)
H	d+π	$59d_{xy}$(61)	d+π	$47d_{xy}$(48)	d+π	$8d_{x2y2}$+$5d_{xy}$(16)
L	π*		π*		π*	
		Pd(II) θ=27º		Pd(II) θ=37º		Pd(II) θ=47º
H	π		π		π	
L	d+π*	$42d_{xy}$(43)	d+π*	$44d_{xy}$(46)	d+π*	$19d_{xy}$+$15d_{x2y2}$(48)
L+1	π*		π*	$6d_{xy}$(6)	π*	
L+2	π*		π*		π*	
L+3	d+π*	$8d_{xy}$(8)	π*		π*	

Table S4 Predictions of free energy of binding (ΔG_{bind}) for two complex.

System	ΔG_{bind} (kcal/mol)	
	Cu(I)_complex	Pd(II)_complex
	-44	-84

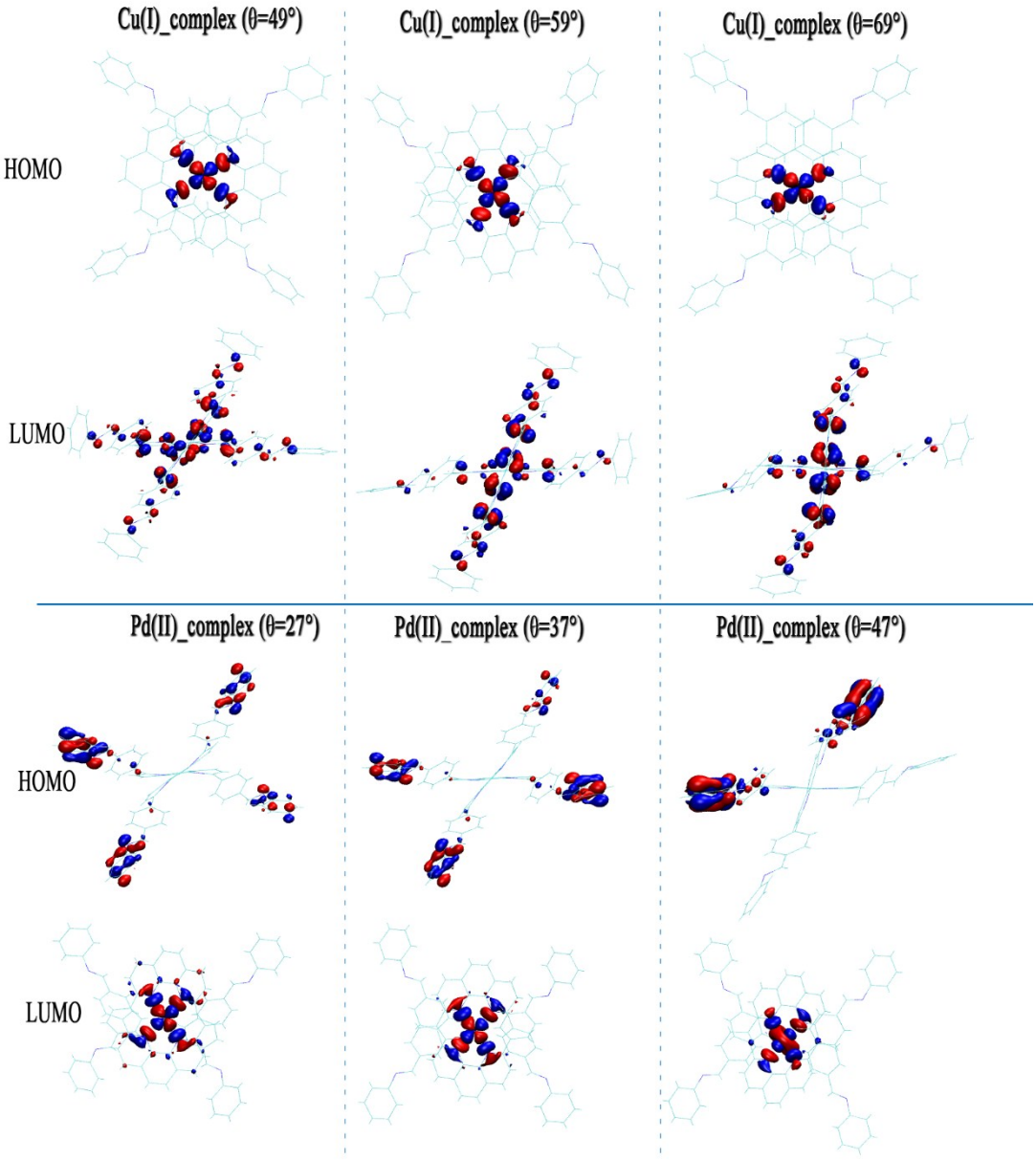

Fig. S3 Frontier orbitals of HOMO and LUMO for different dihedral angles of Cu(I)_complex and Pd(II)_complex. The absolute value of isosurface for all MOs is

0.04. BF_4^- anion are omitted for clarity.

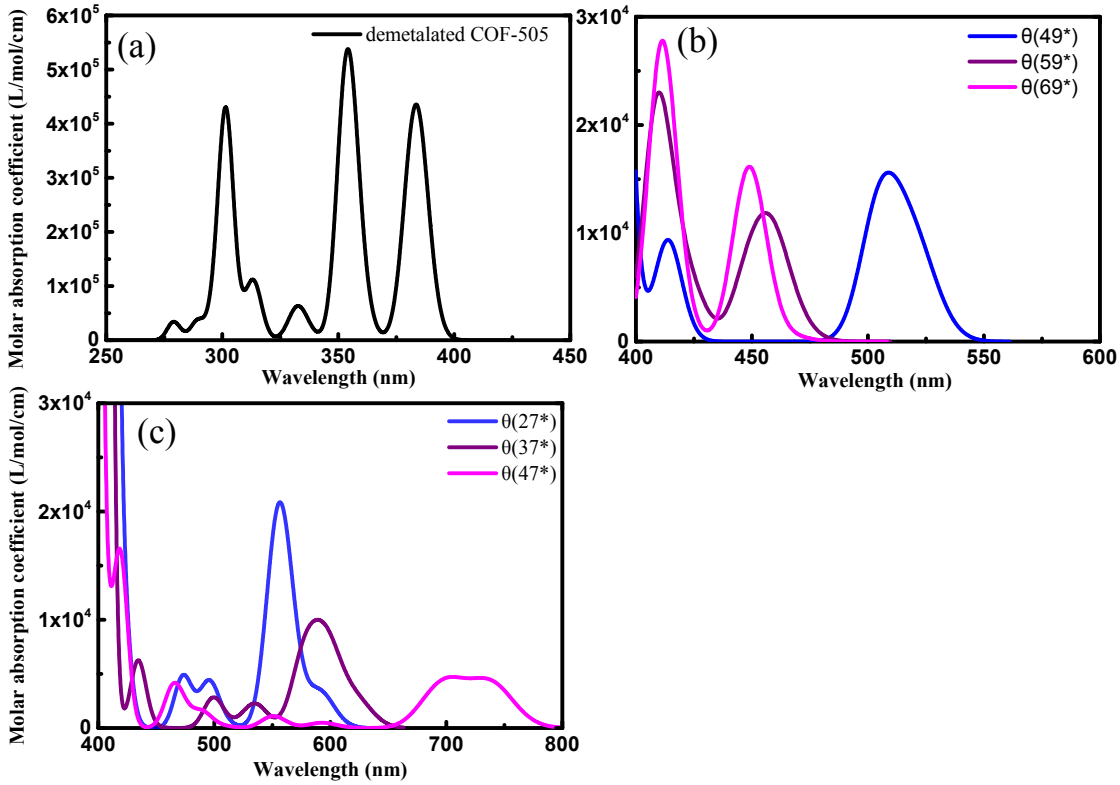

Fig. S4 UV-Vis absorption spectra of (a) demetalated COF-505, (b) Cu(I)_complex with different dihedral angles, (c) Pd(II)_complex with different dihedral angles in dimethylformamide (DMF).

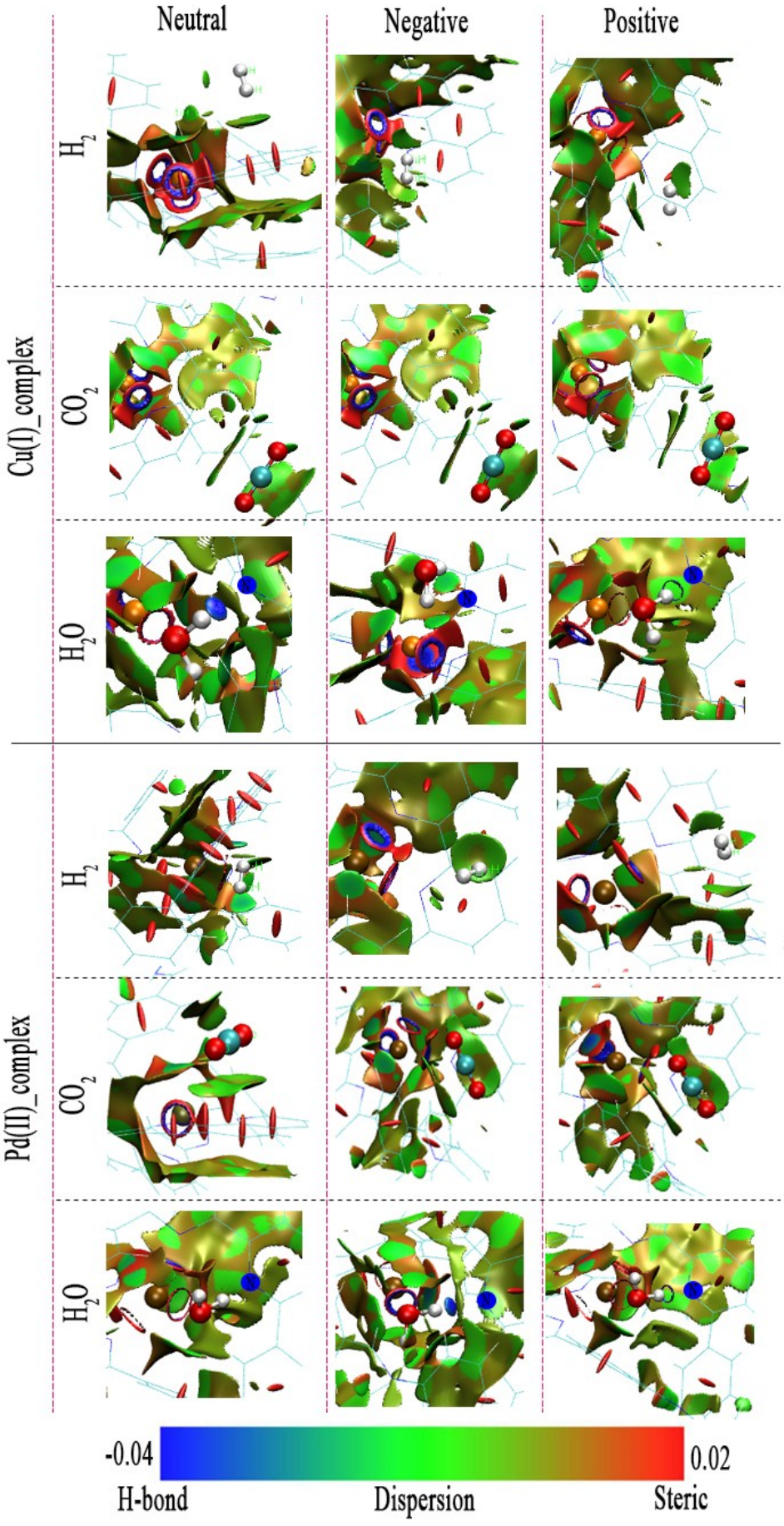
Neutral
Negative
Positive
Cu(I)_complex
Pd(II)_complex
H2
CO2
H2O
-0.04
0.02
H-bond
Dispersion
Steric

Fig. S5 Reduced density gradient isosurface map, isovalue is set to 0.6. The value of Sign(λ_2)ρ in the surface map represented by filling color according to the color bar in the bottom.

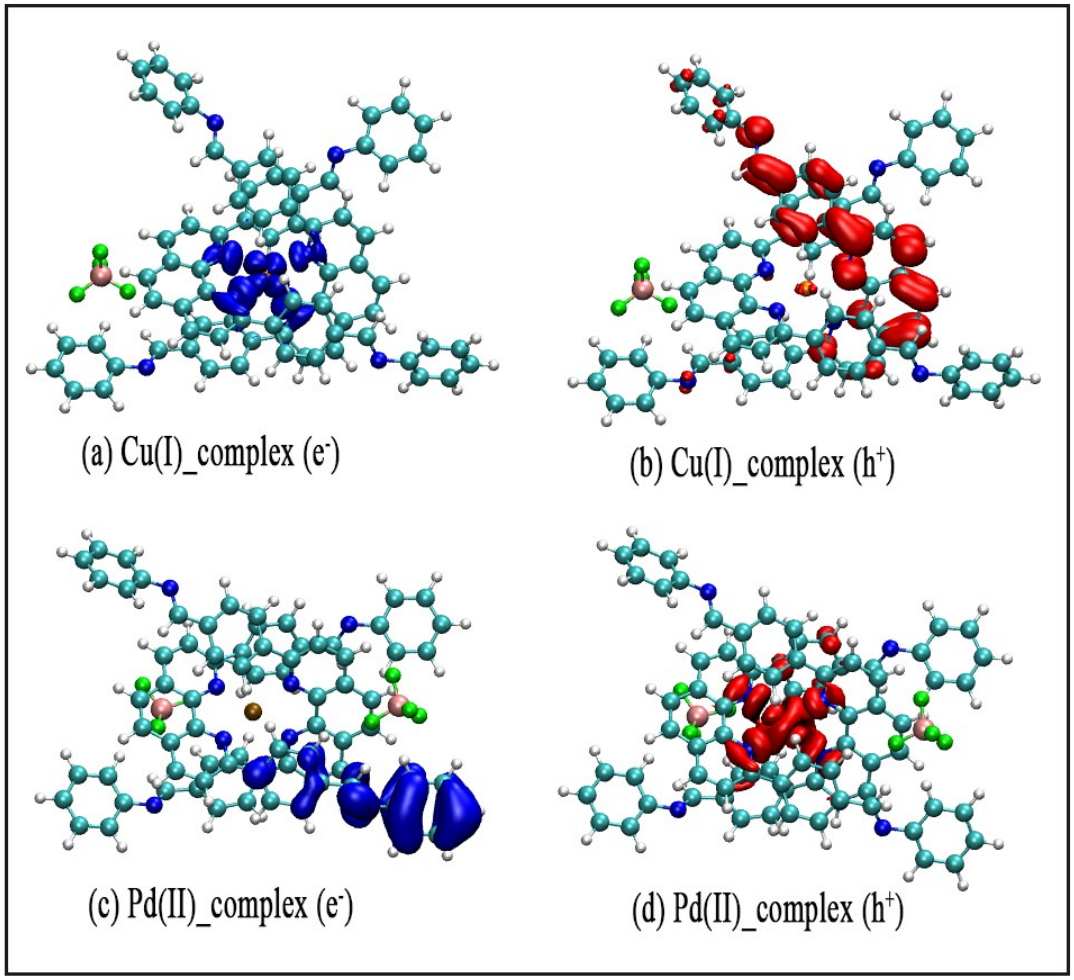

Fig. S6 The density distribution of electron and hole. The absolute value of isosurface for all MOs is 0.04.

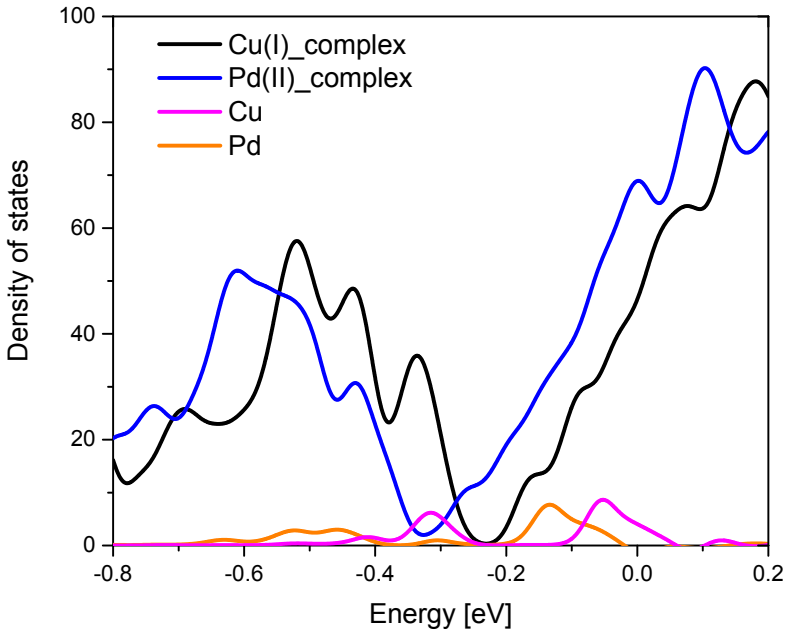

Fig. S7 The total density of states for Cu(I)_complex and Pd(II)_complex and partial density of Cu(I) an Pd(II) atoms.

Table S5 The calculated charge distribution on the neutral, negatively and positively charged complex interacting with the guest molecules by NBO charge analysis. Q_M and Q_x donate the charge of the centered metal and the adsorbed molecules, respectively.

		Neutral		Negative		Positive	
		Q_M	Q_x	Q_M^{Nc}	Q_x	Q_M^{Pc}	Q_x
Cu(I)_complex	H_2	0.488	-0.004	0.454	-0.003	0.744	-0.004
	CO_2	0.513	0.009	0.460	0.014	0.746	0.018
	H_2O	0.534	0.035	0.439	0.088	0.863	0.128
Pd(II)_complex	H_2	0.648	-0.005	0.498	-0.005	0.779	-0.003
	CO_2	0.706	0.019	0.507	0.019	0.763	0.018
	H_2O	0.696	0.016	0.516	0.094	0.857	0.142

1. Y. Z. Liu, Y. H. Ma, Y. B. Zhao, X. X. Sun, F. Gándara, H. Furukawa, Z. Liu, H. Y. Zhu, C. H. Zhu, K. Suenaga, P. Oleynikov, A. S. Alshammari, X. Zhang, O. Terasaki and O. M. Yaghi, *Science*, 2016, **351**, 365–369.

2. P. Wehman, V. E. Kaasjager, F. Hartl, P. C. J. Kamer, P. W. N. M. van Leeuwen, J. Fraanje and K. Goubitz, *Organometallics*, 1995, **14**, 3751–3761.