1. DFT geometry optimized atomic structure

The atomic positions deduced from the DFT geometry optimization are provided in Table S1, including the position of the hydrogen atoms (H1, H2 and H3).

Table S1 : Atomic coordinates corresponding to the DFT geometry optimized model of $[H\mathit{gua}]_2 \cdot (Ti_5O_5F_{12})$

Atom	Site	x	y	z
Ti1	8f	0.41396	0.6837	0.66963
Ti2	2b	½	0	0.55568
F1	8f	0.33269	0.72346	0.61848
F2	8f	0.43678	0.87128	0.61707
F3	4d	0.893	0	0.61681
F4	4e	½	0.6397	0.61357
O1	8f	0.41563	0.69252	0.11898
O2	2b	½	0	0.10915
N1	4d	0.65128	0	0.07887
N2	4d	0.73721	0.88683	0.21856
C	8f	0.70816	0	0.17774
H1	8f	0.77628	0.11363	0.35592
H2	8f	0.7106	0.19244	0.25959
H3	8f	0.62818	0.91499	0.05654

2. Bond valence calculations

The details of the bond valence calculations for the XRD refined and the DFT geometry optimized structures are given in Tables S2 and S3, respectively.

Table S2 : Selected inter-atomic distances d_{ij} (Å) and bond valence s_{ij} (valence units) for the XRD refined structure of $[H\mathit{gua}]_2 \cdot (Ti_5O_5F_{12})$

	$\mathbf{d_{ij}}$	$\mathbf{s_{ij}}$
Ti1-F1	1.856(1)	0.77
Ti1-F2	1.930(1)	0.63
Ti1-F3	1.921(1)	0.65
Ti1-F4	1.957(1)	0.59
Ti1-O1	1.843(1)	0.93
Ti1-O1	1.958(1)	0.68
Ti2-F2 (×4)	1.952(1)	0.60
Ti2-O2	1.699(1)	1.37
Ti2-O2	2.103(1)	0.46
	$\mathbf{S = \sum sij}$	
S(F1) = 0.77	S(F4) = 1.17	S(Ti1) = 4.24
S(F2) = 1.23	S(O1) = 1.61	S(Ti2) = 4.21
S(F3) = 1.29	S(O2) = 1.83	

Table S3 : Selected inter-atomic distances d_{ij} (Å) and bond valence s_{ij} (valence units) for the DFT geometry optimized structure of $[Hgua]_2 \cdot (Ti_5O_5F_{12})$

	$\mathbf{d_{ij}}$	$\mathbf{s_{ij}}$
Ti1-F1	1.876	0.73
Ti1-F2	1.989	0.54
Ti1-F3	1.941	0.61
Ti1-F4	1.991	0.54
Ti1-O1	1.711	1.33
Ti1-O1	2.096	0.47
Ti2-F2 (×4)	1.945	0.61
Ti2-O2	1.697	1.38
Ti2-O2	2.104	0.46
	$\mathbf{S = \sum sij}$	
S(F1) = 0.73	S(F4) = 1.07	S(Ti1) = 4.21
S(F2) = 1.15	S(O1) = 1.79	S(Ti2) = 4.26
S(F3) = 1.23	S(O2) = 1.83	

3. Densities of states

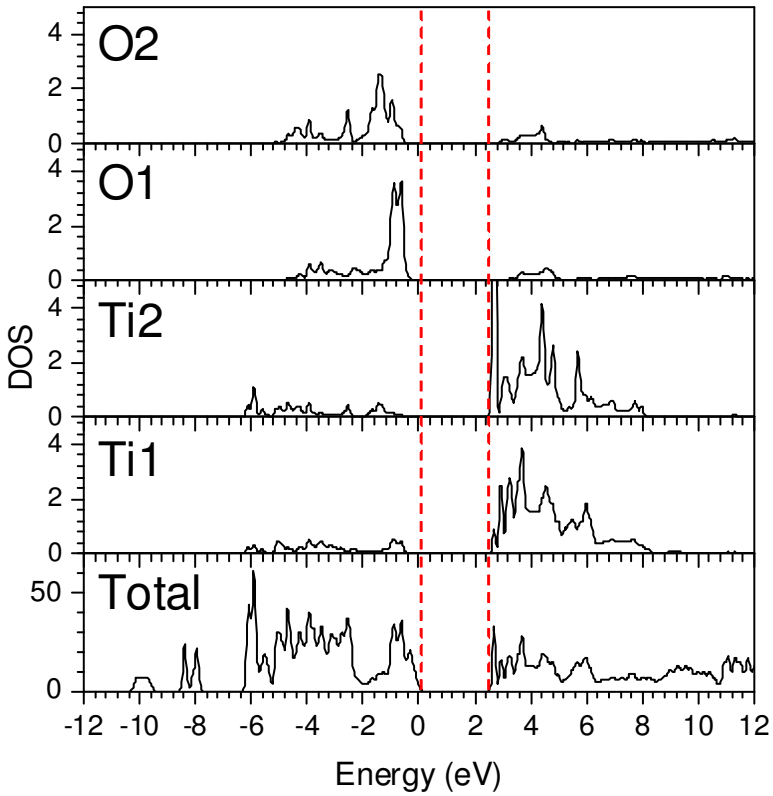

Figure S1. Total and partial (Ti1, Ti2, O1, O2) densities of states of the optimized structure of $[Hgua]_2 \cdot (Ti_5O_5F_{12})$.

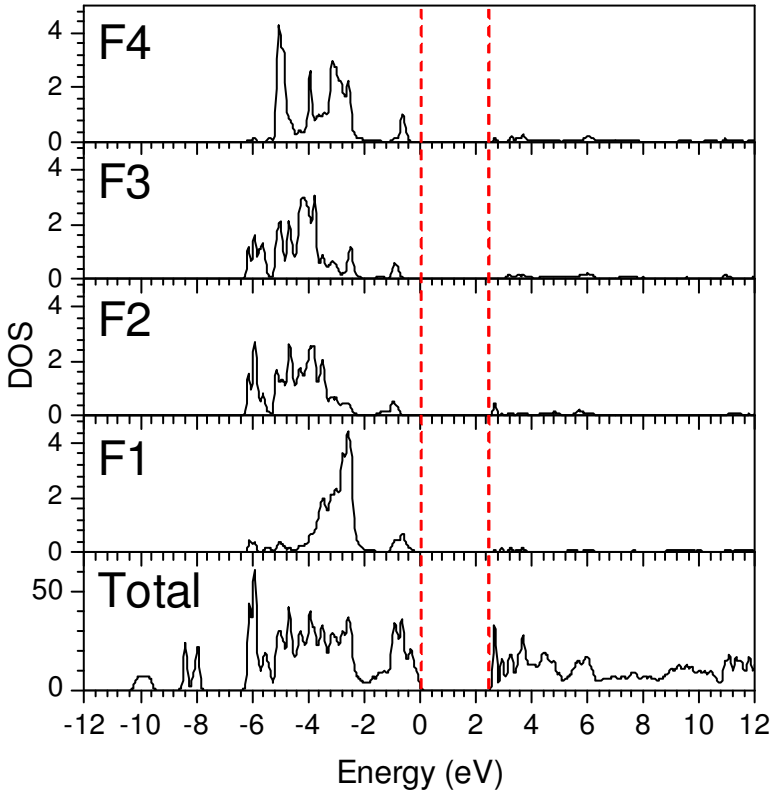

Figure S2. Total and partial (F1, F2, F3, F4) densities of states of the optimized structure of $[Hgua]_2 \cdot (Ti_5O_5F_{12})$.

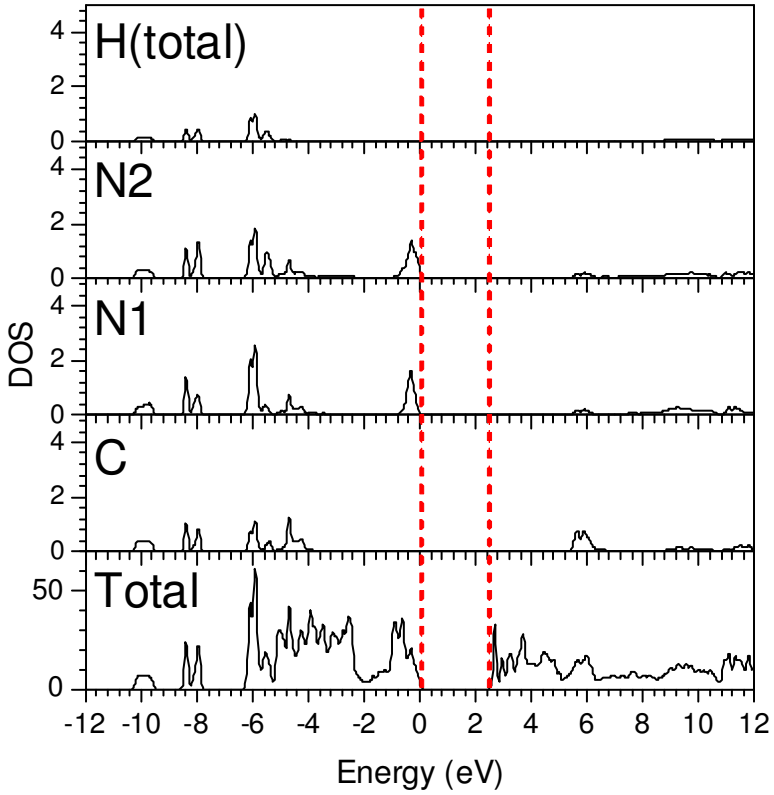

Figure S3. Total and partial (C, N1, N2, H) densities of states of the optimized structure of $[Hgua]_2 \cdot (Ti_5O_5F_{12})$.