Supporting Information

A tetrathiafulvalene grafted titanium-oxo-cluster material: self-catalyzed crystal exfoliation and photocurrent responsive properties

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Tables:

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Table S1. Crystal Data and Structural Refinement Parameters for **TiO-L**

	TiO-L
formula	$C_{124}H_{222}O_{51}S_{24}Ti_{12}$
fw	3873.02
cryst size (mm^3)	0.30 × 0.35 × 0.70
cryst syst	monoclinic
space group	$P\,2_1/n$
a (Å)	21.0421(17)
b (Å)	32.775(3)
c (Å)	28.371(2)
α (deg)	90.00
β (deg)	91.981(2)
γ (deg)	90.00
V ($Å^3$)	19554(3)
Z	4
ρ_{calcd} ($g\ cm^{-3}$)	1.313
F(000)	8056
μ (mm^{-1})	0.784
T (K)	293(2)
reflns collected	76824
unique reflns	33700
observed reflns	17016
no. params	1909
GOF on F^2	1.035
R_1 [I>2σ(I)]	0.1138
${}_wR_2$ [I>2σ(I)]	0.1603

Table S2. The calculated energy levels (eV) of compounds **TiO-L** and **TiO-BDC**.

	TiO-L	**TiO-**BDC
LUMO+3	–2.32032	–1.96085
LUMO+2	–2.38154	–2.15541
LUMO+1	–2.47515	–2.24195
LUMO	–2.53284	–2.29773
HOMO	–5.33724	–6.99551
HOMO–1	–5.38378	–7.12803
HOMO–2	–6.62108	–7.18871
HOMO–3	–6.63659	–7.31633

Table S3. Theoretical and experimental Ti–O and Ti–Ti bond lengths (Å) in **TiO-L** and **TiO-BDC**.

TiO-L			**TiO-BDC**		
bond	exp	theory	bond	exp	theory
Ti7–O26	2.080	2.033	Ti1–O6	2.179	2.176
Ti7–O31	2.198	2.191	Ti2–O13	2.064	2.020
Ti8–O30	2.204	2.215	Ti3–O12	2.047	2.003
Ti9–O27	2.081	2.033	Ti3–O7	2.140	2.119
Ti10–O28	2.113	2.107	Ti4–O8	2.020	1.999
Ti10–O32	2.046	2.000	Ti4–O14	2.103	2.115
Ti11–O33	2.068	2.043	Ti5–O15	2.183	2.178
Ti12–O29	2.195	2.244	Ti6–O9	2.060	2.027
Ti7–Ti8	3.150	3.178	Ti1–Ti2	3.102	3.145
Ti8–Ti9	3.105	3.147	Ti1–Ti3	3.151	3.187
Ti10–Ti12	3.155	3.192	Ti4–Ti5	3.131	3.183
Ti11–Ti12	3.097	3.143	Ti5–Ti6	3.089	3.147

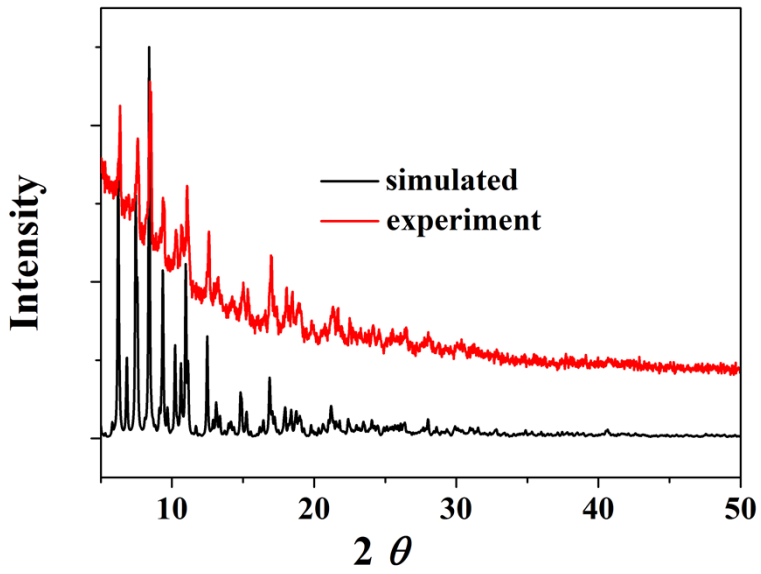


Figure S1. The experimental powder XRD pattern and the simulated pattern from the red crystal data of compound **TiO-L**.

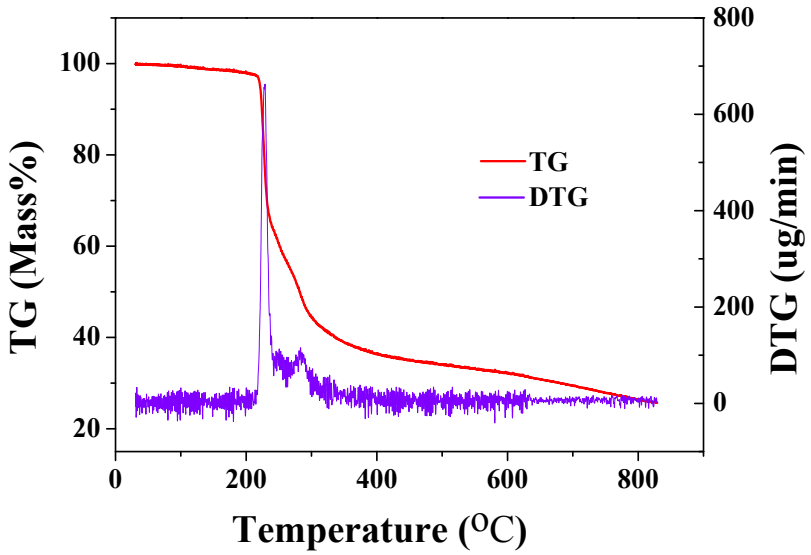


Figure S2. TG and DTG curves of red crystal **TiO-L**.

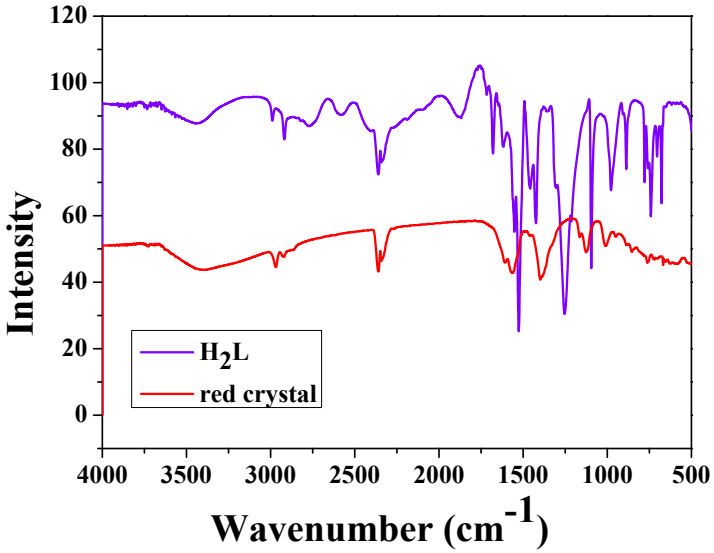


Figure S3. FTIR spectra of red crystal **TiO-L** and the ligand **H_2L**.

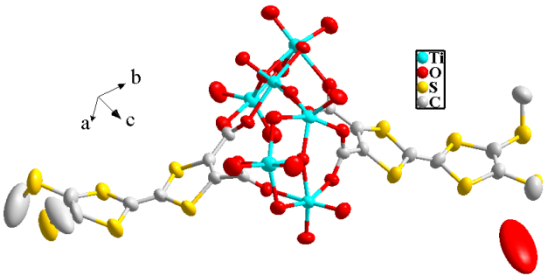


Figure S4. Molecular structure of complex **TiO-L** with 30% thermal probability.

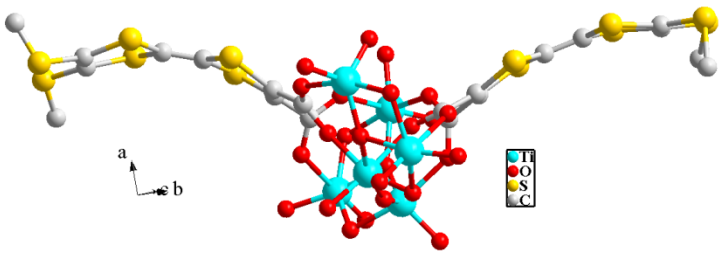


Figure S5. View of the **TiO-L** cluster showing the unique two wing-like TTF groups.

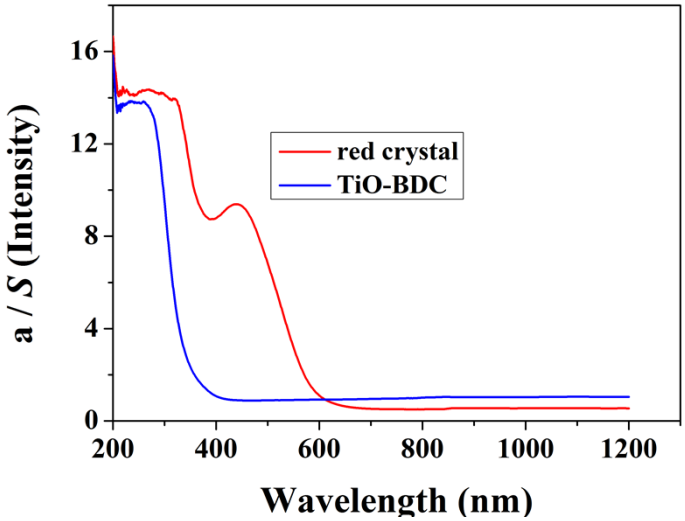


Figure S6. UV-vis-NIR absorption spectra of the red crystal **TiO-L** and the colorless crystal **TiO-BDC**.

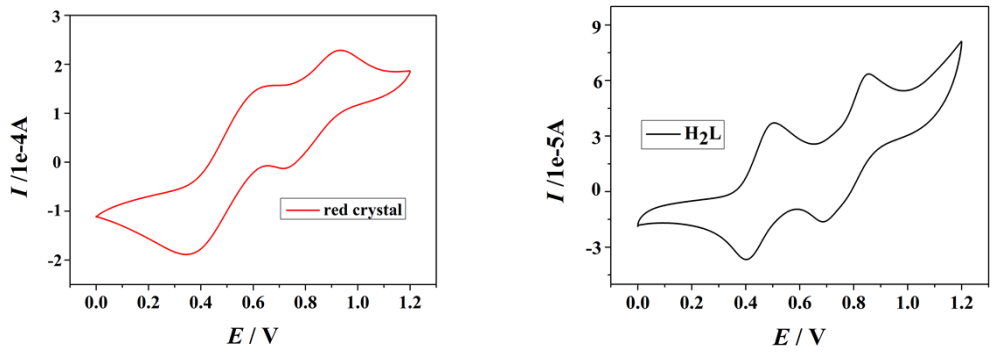


Figure S7. Cyclic voltammogram of the red crystal **TiO-L** (left) and H_2L (right) in DMF/CH_2Cl_2 (1:4 by volume) (0.1 mol·L^{-1} Bu_4NClO_4, 100 mV s^{-1}).

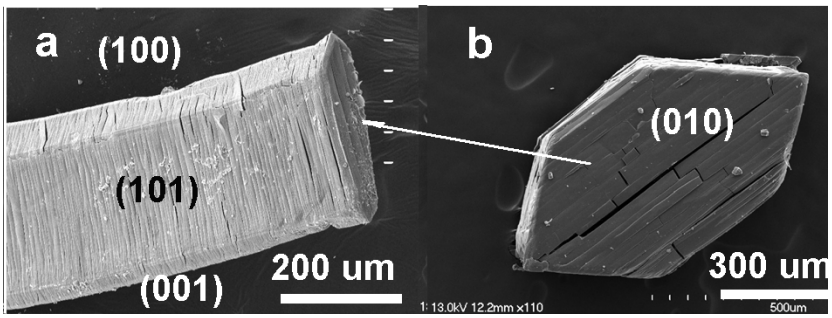


Figure S8. (a) Layered structure appeared on (101), (001), and (100) faces of the blackened crystal. (b) floor-board-like plates observed on (010) face.

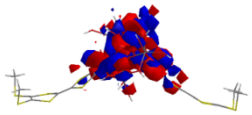
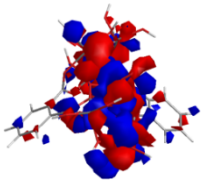
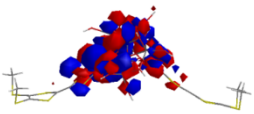
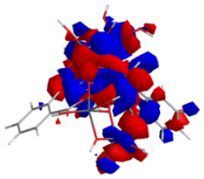
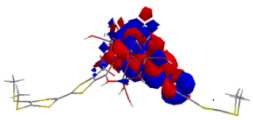
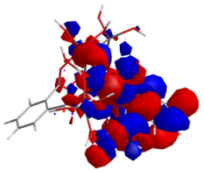
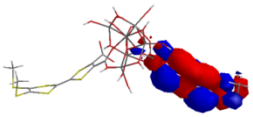
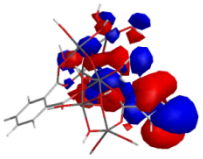
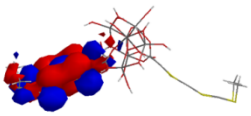
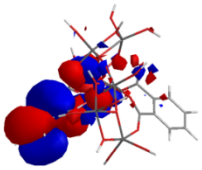
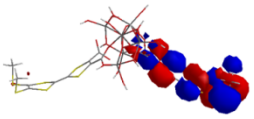
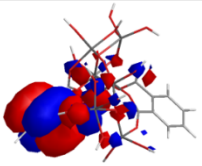
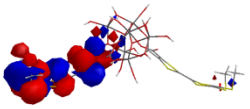
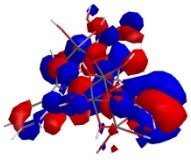
	TiO-L	**TiO-BDC**
LUMO+2		
LUMO+1		
LUMO		
HOMO		
HOMO–1		
HOMO–2		
HOMO–3		

Figure S9. Calculated electronic densities for the frontier orbitals of **TiO-L** and **TiO-BDC**. Titanium atoms are gray; oxygen, red; carbon, pale-gray; and sulfur, yellow.