

Supporting Information

Phenanthroline-Mediated Photoelectrical Enhancement in Calix[4]arene-Functionalized Titanium-Oxo Clusters

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Figure S1. The compared PXRD patterns of Ti2.

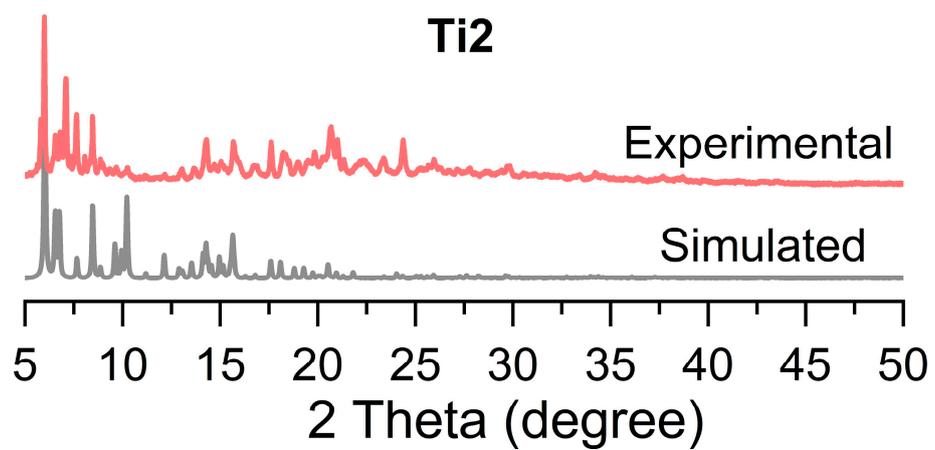


Figure S2. The compared PXRD patterns of Ti₂-Phen.

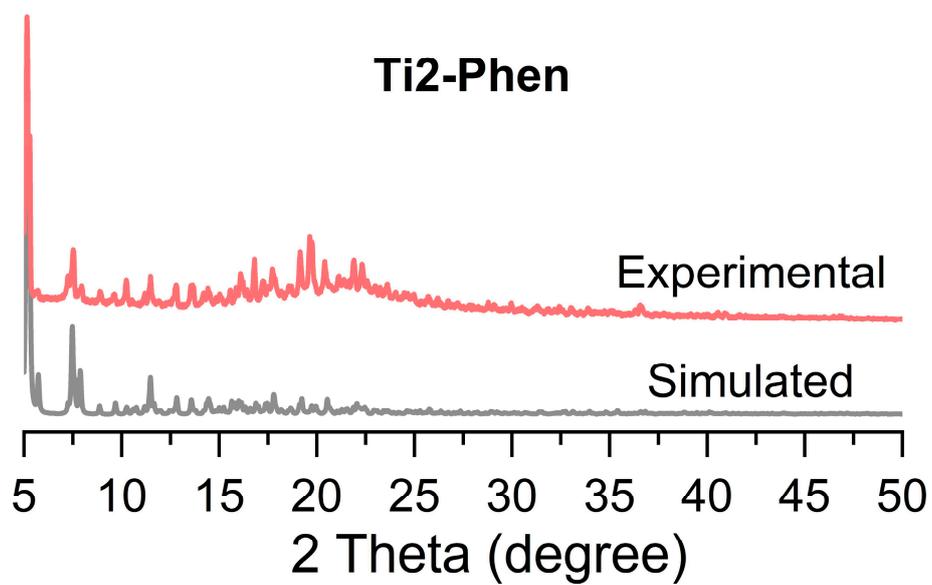


Figure S3. The compared PXRD patterns of Ti₂-BPhen.

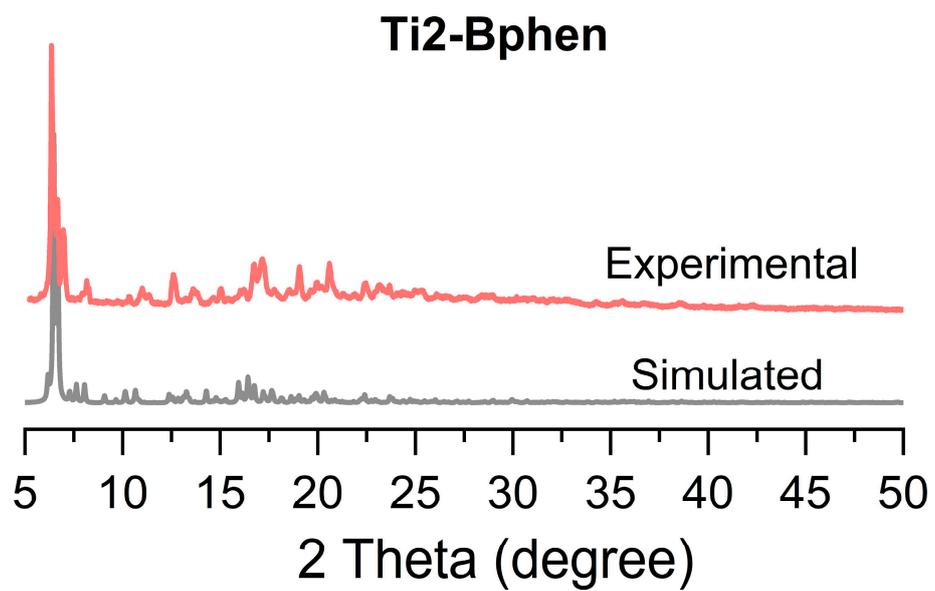


Figure S4. The Fourier transform infrared spectroscopy (FT-IR) of **Ti2**, **Ti2-Phen**, and **Ti2-Bphen**.

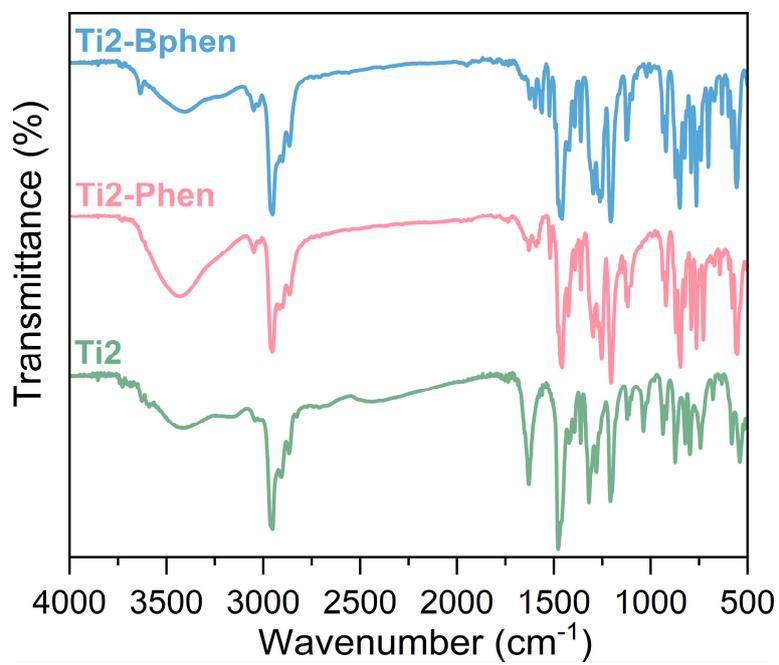


Figure S5. Elemental mapping images of Ti, O, and C of selected area for **Ti2**.

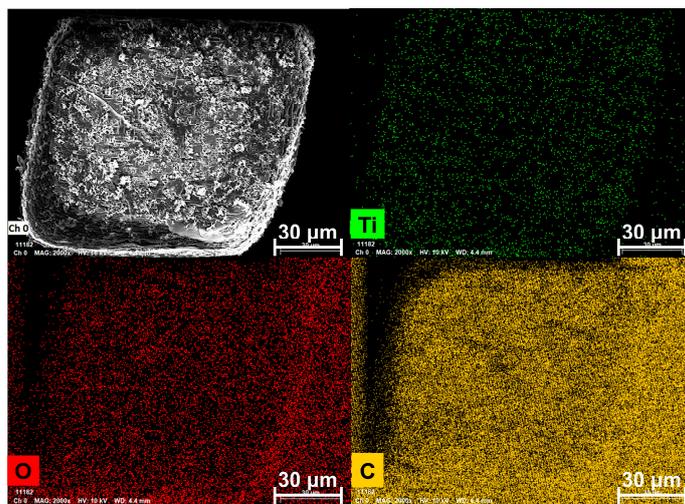


Figure S6. Elemental mapping images of Ti, O, and N of selected area for **Ti2-Phen**.

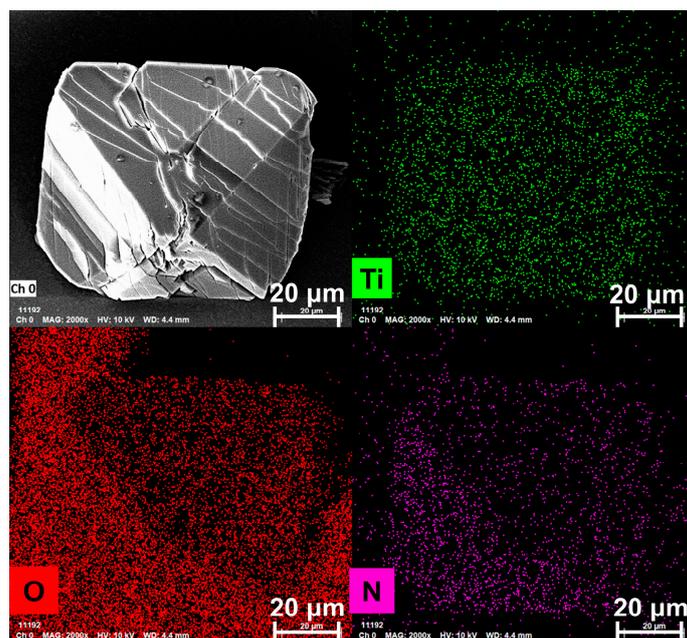


Figure S7. Elemental mapping images of Ti, O, and N of selected area for **Ti2-Bphen**.

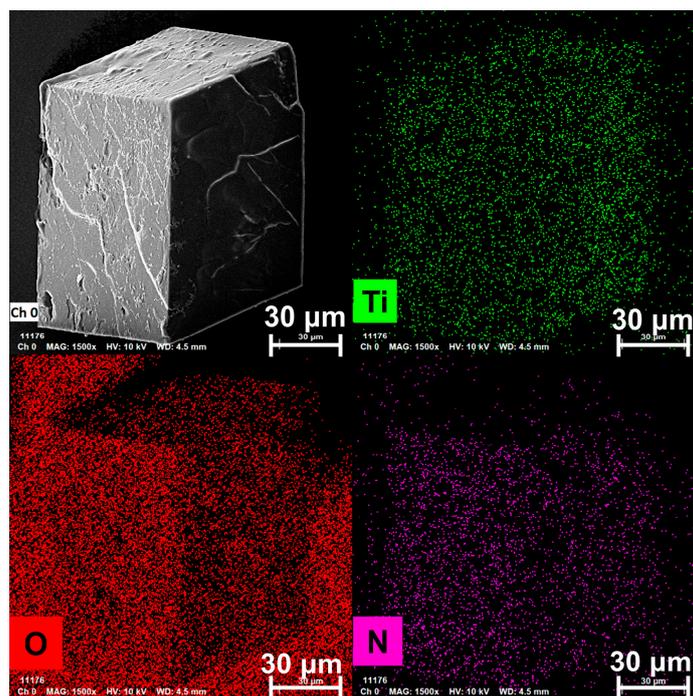


Figure S8. X-ray photoelectron spectroscopy (XPS) spectra of **Ti2**.

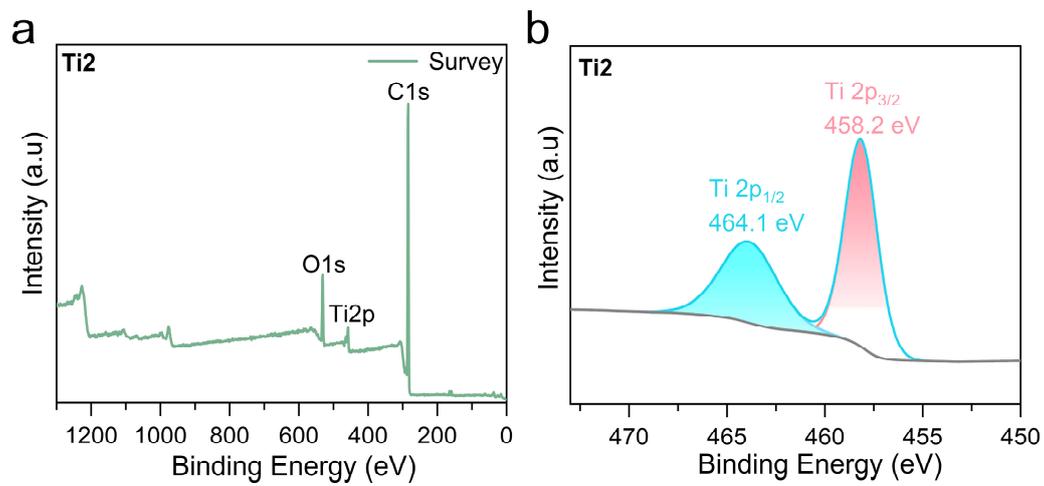


Figure S9. X-ray photoelectron spectroscopy (XPS) spectra of **Ti2-Phen**.

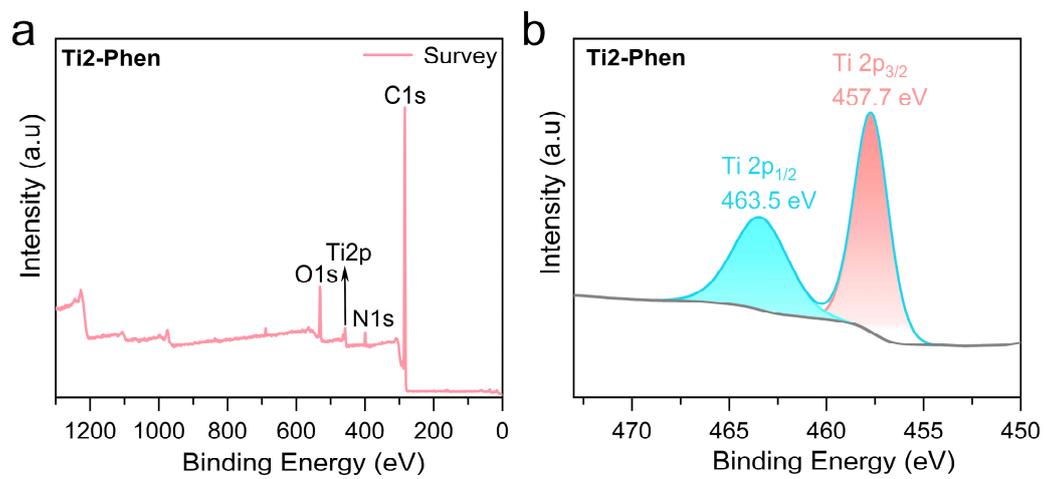


Figure S10. X-ray photoelectron spectroscopy (XPS) spectra of **Ti2-Bphen**.

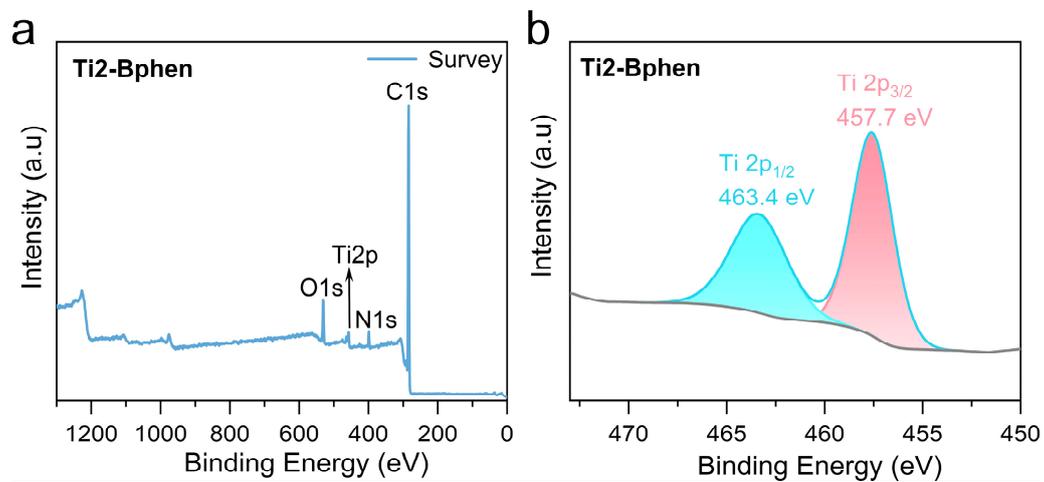


Figure S11. PXRD patterns of **Ti2-Bphen** immersed in water solutions with pH values of 1, 7, and 11 for 24 hours.

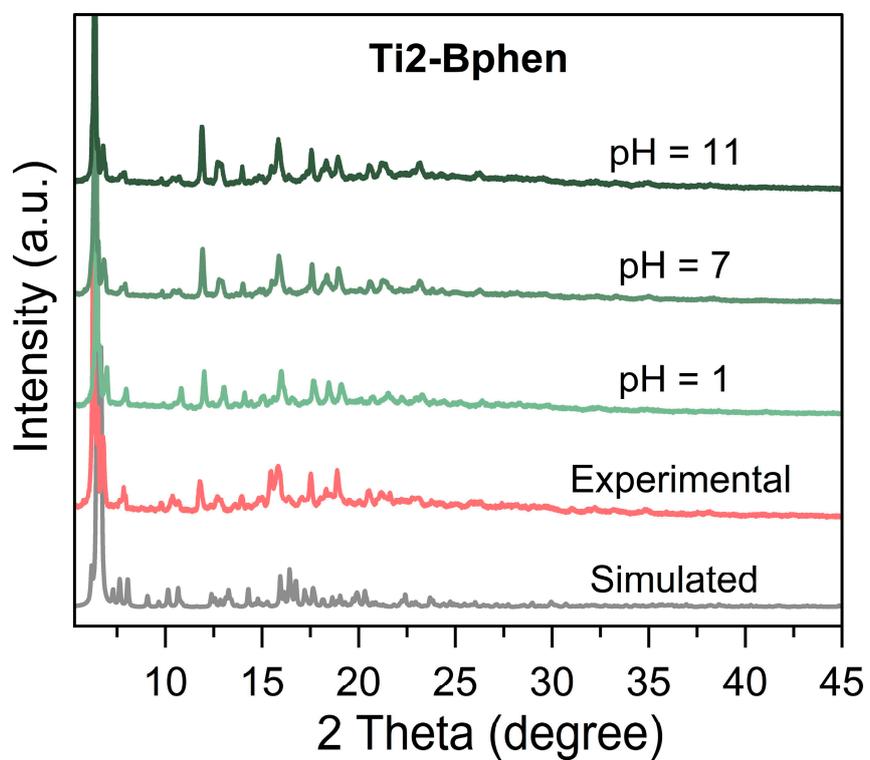


Figure S12. The thermogravimetric analysis (TGA) curves of **Ti2**, **Ti2-Phen**, and **Ti2-Bphen**.

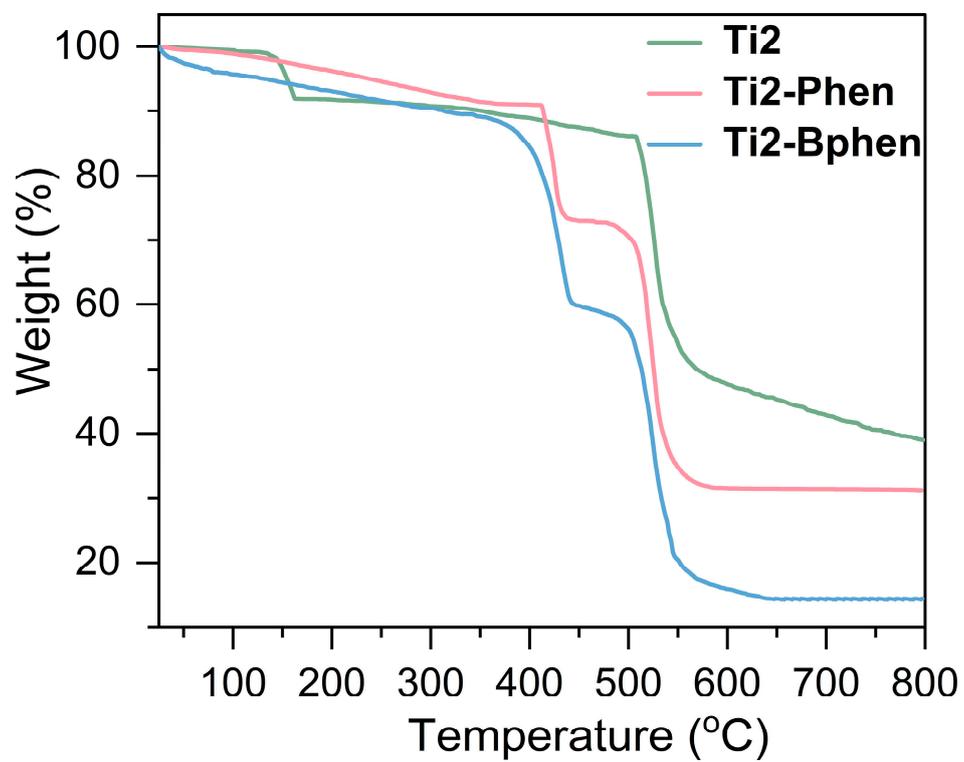


Figure S13. The PXRD patterns of **Ti₂-Phen** before and after photocurrent testing.

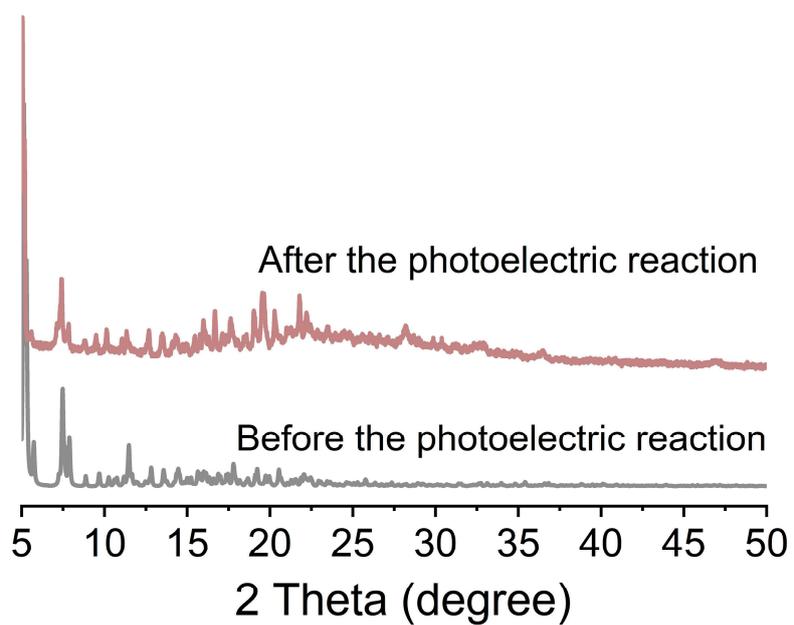


Figure S14. The six cycles of photocurrent testing of **Ti2-Phen**.

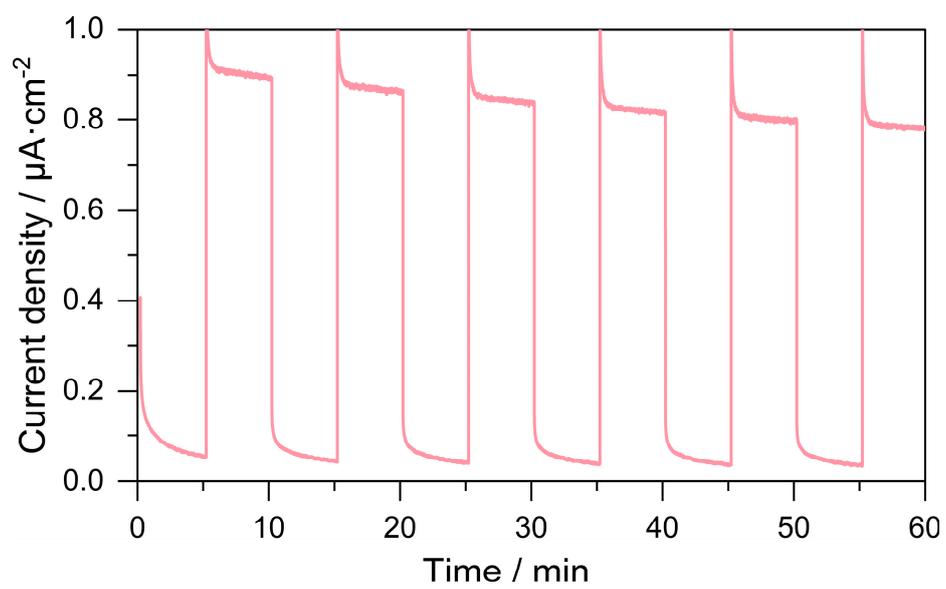


Table S1. Exploration of the synthesis of **Ti2-Phen**.

TBC4A (mmol)	Phen (mmol)	Ti(ⁱ PrO) ₄ (mmol)	Solvent (5 mL)	Temperature (°C)	Result
0.10	0.30	0.66	isopropanol	100	√
0.10	0.30	0.66	isopropanol	80	×
0.10	0.30	0.66	methanol	100	×
0.10	0.30	0.66	ethanol	100	×
0.10	0.30	0.66	acetonitrile	100	×

Table S2. Crystal data collection and structure refinement for **Ti2**, **Ti2-Phen**, and **Ti2-Bphen**.

Compound	Ti2	Ti2-Phen	Ti2-Bphen
Empirical formula	C ₉₀ H ₁₁₀ O ₁₀ Ti ₂	C ₁₁₂ H ₁₂₀ N ₄ O ₈ Ti ₂	C ₁₃₆ H ₁₃₆ N ₄ O ₈ Ti ₂
Formula weight	1447.57	1745.90	2050.29
Temperature [K]	293.0	173.0	173.0
Crystal system	triclinic	monoclinic	monoclinic
Space group (number)	$P\bar{1}$ (2)	$C2/c$ (15)	$C2/m$ (12)
<i>a</i> [Å]	13.2106(13)	45.092(12)	28.604(7)
<i>b</i> [Å]	14.0049(14)	19.851(6)	21.949(3)
<i>c</i> [Å]	15.2780(15)	30.826(8)	21.140(4)
α [°]	104.353(5)	90	90
β [°]	95.764(3)	130.034(10)	92.837(10)
γ [°]	94.865(2)	90	90
Volume [Å ³]	2706.9(5)	21126(10)	13256(5)
<i>Z</i>	1	4	2
ρ_{calc} [g/cm ³]	0.888	1.117	1.027
μ [mm ⁻¹]	0.190	1.718	1.425
<i>F</i> (000)	774	7560	4352
Radiation	MoK α ($\lambda=0.71073$ Å)	CuK α ($\lambda=1.54178$ Å)	CuK α ($\lambda=1.54178$ Å)
2 θ range [°]	4.09 to 50.04 (0.84 Å)	5.74 to 134.15 (0.84 Å)	5.08 to 134.32 (0.84 Å)
Index ranges	-15 ≤ <i>h</i> ≤ 15 -12 ≤ <i>k</i> ≤ 16 -18 ≤ <i>l</i> ≤ 11	-53 ≤ <i>h</i> ≤ 53 -23 ≤ <i>k</i> ≤ 23 -36 ≤ <i>l</i> ≤ 34	-34 ≤ <i>h</i> ≤ 32 -26 ≤ <i>k</i> ≤ 26 -24 ≤ <i>l</i> ≤ 25
Reflections collected	13255	85697	61763
Independent reflections	9389 <i>R</i> _{int} = 0.0808 <i>R</i> _{sigma} = 0.1366	18826 <i>R</i> _{int} = 0.0371 <i>R</i> _{sigma} = 0.0288	12080 <i>R</i> _{int} = 0.0664 <i>R</i> _{sigma} = 0.0505
Completeness	98.2 %	99.7 %	98.9 %
Data / Restraints / Parameters	9389/360/566	18826/809/1415	12080/668/871
Goodness-of-fit on <i>F</i> ²	1.137	1.063	1.411
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.1007 <i>wR</i> ₂ = 0.2511	<i>R</i> ₁ = 0.0420 <i>wR</i> ₂ = 0.1159	<i>R</i> ₁ = 0.1097 <i>wR</i> ₂ = 0.3349
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1671 <i>wR</i> ₂ = 0.2778	<i>R</i> ₁ = 0.0489 <i>wR</i> ₂ = 0.1211	<i>R</i> ₁ = 0.1329 <i>wR</i> ₂ = 0.3554
Largest peak/hole [e/Å ³]	0.63/-0.53	0.43/-0.43	0.95/-1.41

Table S3. Comparison of crystallographic parameters for **Ti2** and **Ti2-MeOH**.

Compound	Ti2	Ti2-MeOH
Crystal system	triclinic	monoclinic
Space group	<i>P</i> -1	<i>P</i> 2 ₁ /n
<i>a</i> [Å]	13.2106	19.8135
<i>b</i> [Å]	14.0049	22.9853
<i>c</i> [Å]	15.2780	23.1531
α [°]	104.353	90
β [°]	95.764	102.0212
γ [°]	94.865	90
Volume [Å ³]	2706.85	10313.1

Table S4. Comparison of synthesis details for **Ti2** and **Ti2-MeOH**.

Compound	Ti2	Ti2-MeOH
TBC4A (mmol)	0.10	0.032
Ti(O ⁱ Pr) ₄ (mmol)	0.66	0.33
MeOH (mL)	3	3
DMF (mL)	2	0
reaction temperature (°C)	100	80
reaction time (d)	5	2