

Electronic Supplementary Information for

**Microporous Organic Nanorods with Electronic Push-Pull Skeleton
for Visible Light-Induced Hydrogen Evolution from Water**

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Experimental Sections

Scanning (SEM) and transmission electron microscopy (TEM) images were obtained using a FE-SEM (JSM6700F) and a JEOL 2100F unit. The adsorption-desorption isotherm for N₂ (77 K) was recorded using BELSORP II-mini volumetric adsorption equipment. Powder X-ray diffraction (PXRD) patterns were obtained using a Rigaku MAX-2200. The reflectance and emission spectra were obtained by Shimadzu UV-3600 and JASCO FP-6200 spectrofluorometer. The solid phase ¹³C-NMR spectrum was obtained on a Bruker 400 MHz DSX NMR spectrometer at the Korea Basic Science Institute (Daegu). The IR spectrum was obtained by Bruker Vertex 70. The thermogravimetric analysis (TGA) curve was obtained by Seiko Exstar 7300. Elemental analysis was performed on a CE EA1110 instrument.

Synthetic procedure of VH-MON

The tris(4-formylphenyl)amine and [1,1'-biphenyl]-4,4'-diacetonitrile were prepared according to the procedures in the literature.(ref. 17 and 18 in text) In a 50 mL Schlenk flask, tris(4-formylphenyl)amine (0.12 mmol, 39 mg) and [1,1'-biphenyl]-4,4'-diacetonitrile (0.18 mmol, 42 mg) were dissolved in THF (24 mL). To this solution, NaOH (0.12 mmol, 5.0 mg) was added. After heating at 70°C for 24 hours, the resulting precipitates were retrieved by centrifugation, washed with water, methanol, methylene dichloride, and acetone, and dried under vacuum.

Synthetic procedure for VH-MON/TiO₂-Pt, eosin Y/TiO₂-Pt, and N719/TiO₂-Pt composites

For the preparation of TiO₂-Pt composite (ref. 22 in text), TiO₂ (2.0 g, Aldrich No. 637254, particle size < 25 nm, anatase) was dispersed in 50 mL methanol using a 100 mL round-bottomed flask. H₂PtCl₆ (0.50 mL, 8 wt% aqueous solution) was added to the solution. Using a 200 W Xe lamp (without an optical filter, 10.0 mW/cm² intensity), the reaction mixture was irradiated for 30 minutes. The resultant TiO₂-Pt composite was retrieved by centrifugation with a 3700 rpm rate, washed five times with excess methanol and dried under vacuum. For the preparation of **VH-MON**/TiO₂-Pt composite, the TiO₂-Pt (30 mg) in 20 mL methanol was treated for 30 minutes by ultrasound processor (Branson Sonifier 450, 400 W, 20 kHz, 100% vibration amplitude, 50% duty cycle, cylindrical titanium alloy probe). To the suspension, the **VH-MON** (30 mg) was added. The mixture was refluxed for 18 hours in the dark. The resultant **VH-MON**/TiO₂-Pt composite was retrieved by centrifugation, washed with methanol, and dried under vacuum. For the preparation of eosin Y/TiO₂-Pt, and N719/TiO₂-Pt composites, the dyes (0.30 mM) were dissolved in 20 mL methanol. The TiO₂-Pt powder (0.20 g) was added. The solution was

stirred for 24 hours at room temperature in the dark. The resultant dye/TiO₂-Pt composites were retrieved by centrifugation, washed with methanol, and dried under vacuum.

Photocatalytic test procedure

The triethanolamine (TEOA) was used as an electron sacrifier. First, a 10% (v/v) TEOA aqueous solution was prepared and neutralized with HCl and NaOH solution. The solution (3 mL) and spin bar were added to tube type glassware. **VH-MON**/TiO₂-Pt, eosin Y/TiO₂-Pt, or N719/TiO₂-Pt composites (8 mg) were added and dispersed in glassware. After sealing the glassware with a septum and insulating tape completely, the solution was bubbled with N₂ gas for 15 minutes using a needle and a connected bubbler. Then, 1 mL N₂ gas was replaced with 1 mL methane (internal standard) using a gas chromatography (GC) syringe. The solution was stirred and irradiated with a 200 W Xe lamp (with an optical filter to cut off the light with wavelengths shorter than 420 nm, 4.6 mW/cm² intensity). The temperature of the reaction mixture was maintained at room temperature with a water bath. The amount of hydrogen generated was measured using GC (Agilent 6890) with a thermal conductivity detector (TCD). It should be noted that the TCD detector has different detection sensitivities toward methane and hydrogen. The detection sensitivity of the GC used for methane and hydrogen was calibrated by the average value from ten data points obtained using the same amount of methane and hydrogen.

Figure S1. SEM images of organic materials obtained using the different volumes of solvent (THF).

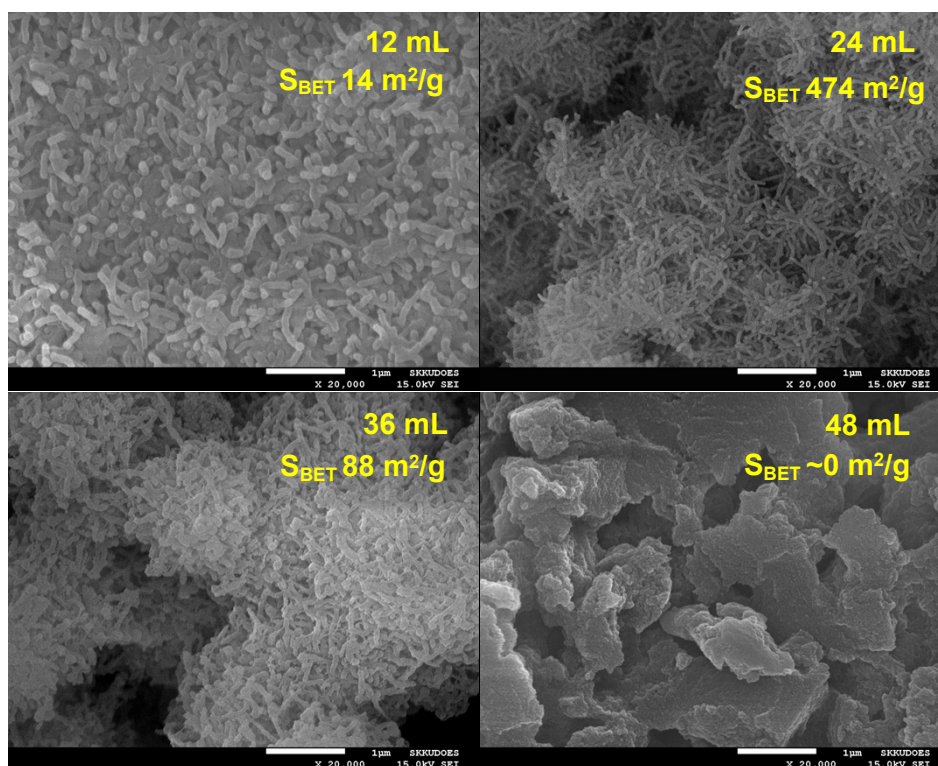


Figure S2. Low magnification-SEM image of **VH-MON**.

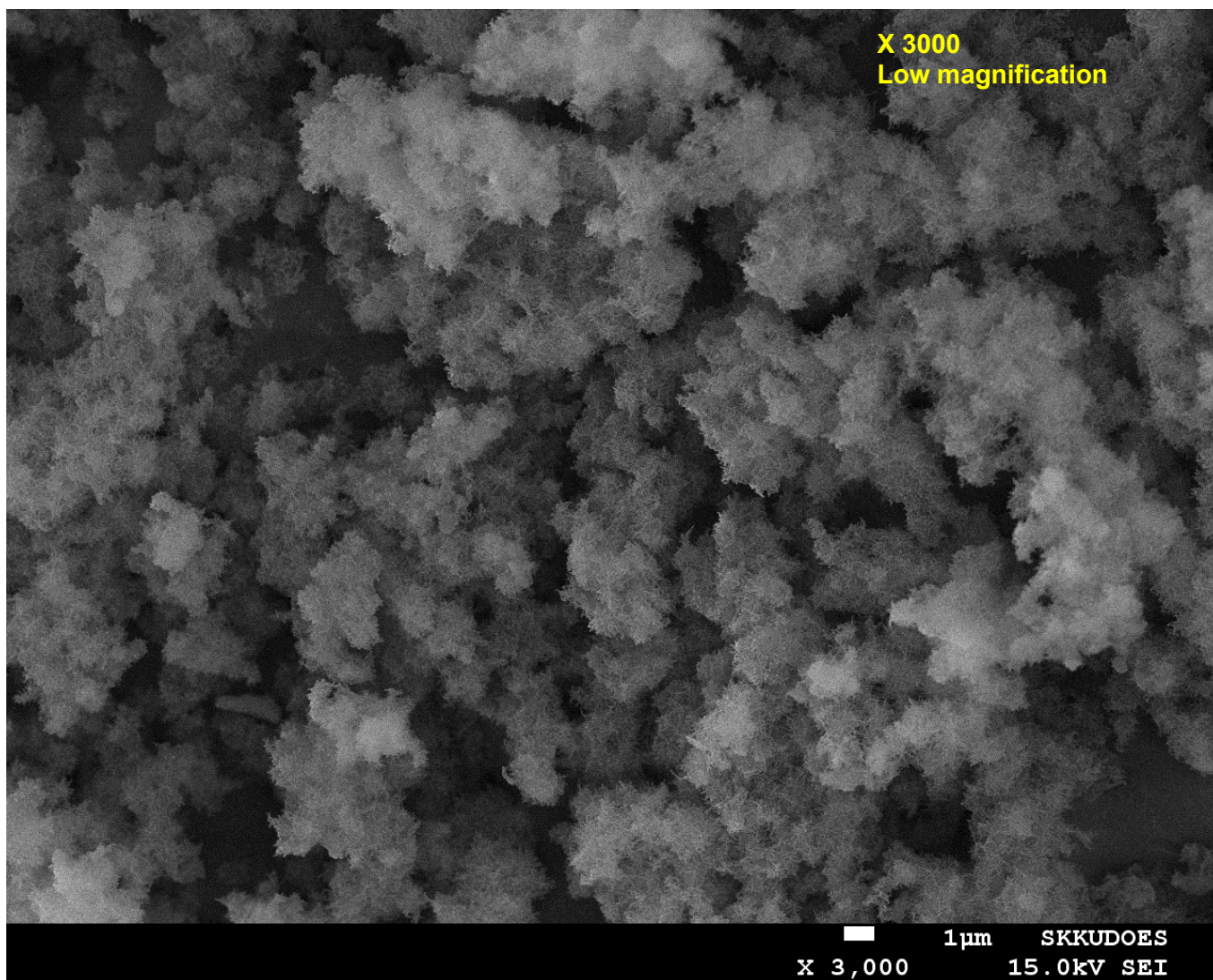


Figure S3. Thermogravimetric analysis of **VH-MON**.

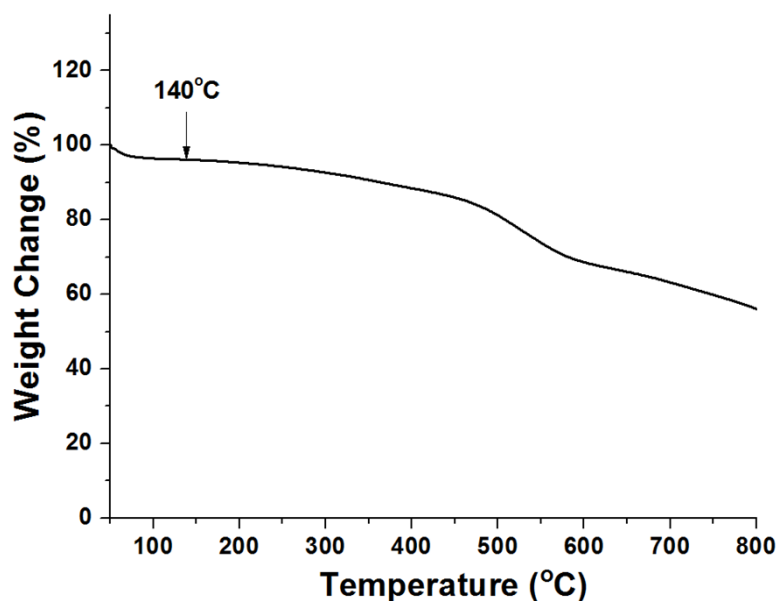
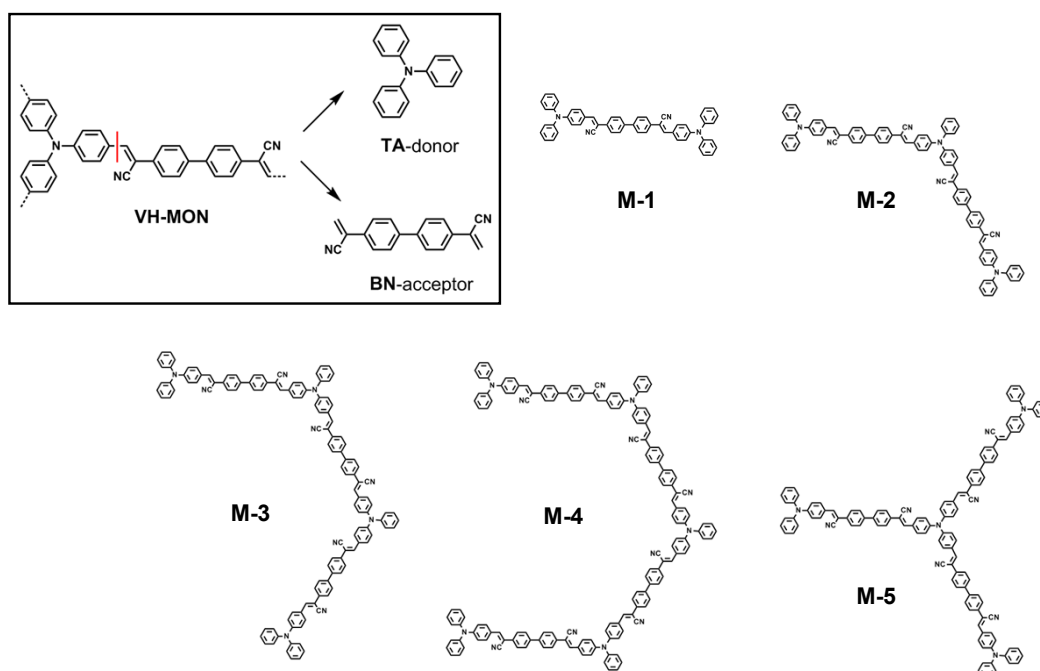
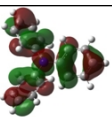
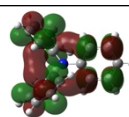

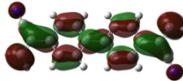
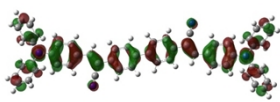
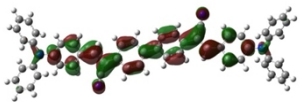
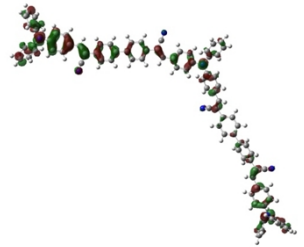
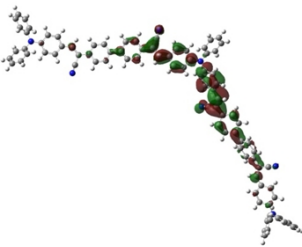
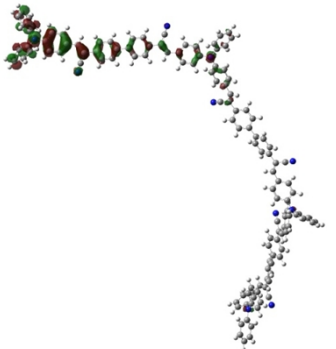
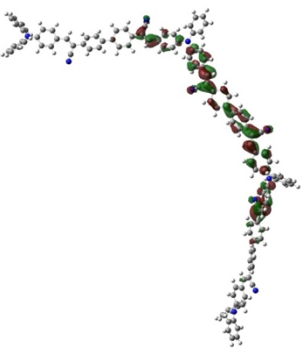


Table S1. B3LYP/6-31G* calculated HOMO-LUMO energy levels with Gaussian 09 programs (M. J. Frisch, *et al.*, *Gaussian 09, Revision B.01*, Gaussian, Inc., Wallingford CT, 2009) of the frontier molecular orbitals of model compounds (**TA-Donor**, **BN-Acceptor**, and **M-1~5**) and triethanolamine (TEOA).



Compounds	HOMO (eV)	LUMO (eV)
TA-Donor	-4.95	-0.30
BN-Acceptor	-6.34	-2.21
M-1	-5.04	-2.08
M-2	-5.09	-2.31
M-3	-5.10	-2.37
M-4	-5.10	-2.39
M-5	-5.11	-2.39
TEOA	-4.99	1.88

Figure S4. B3LYP/6-31G* calculated HOMO and LUMO figures of model compounds (TA-Donor, BN-Acceptor, and M-1~5).

	HOMO	LUMO
TA-Donor		
BN-Acceptor		
M-1		
M-2		
M-3		

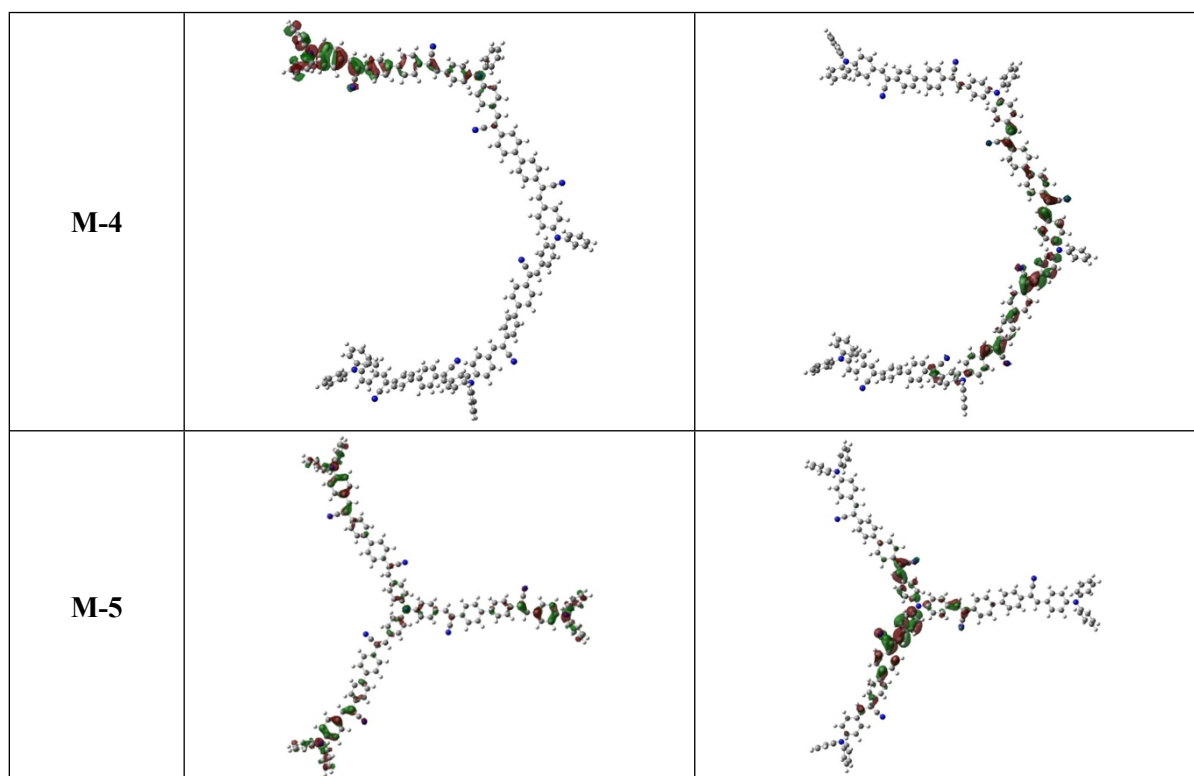


Figure S5. Cartesian coordinates (in Å) of model compounds (TA-Donor, BN-Acceptor, and M-1~5) and TEOA.

TA-Donor			C	-2.94655800	0.89725400	-0.35036100	C	-5.91680000	-0.02157500	-0.06567000	
N	0.00019700	-0.00011400	-0.00237200	H	-1.10980600	1.95063700	-0.66781700	C	-4.97636600	-0.99368000	-0.26208800
C	-0.62171800	1.27826300	-0.00066100	C	-2.74969500	-1.38425400	0.39413000	H	-5.50784300	0.96924700	0.12016500
C	-1.74882600	1.52292900	0.80085300	H	-0.76173900	-2.10312600	0.72515100	C	-3.52015100	-0.70093900	-0.29247900
C	-0.11943800	2.31709300	-0.80144600	C	-3.56793200	-0.30832200	0.01123600	C	-5.33120800	-2.37230300	-0.42078000
C	-2.36078600	2.77483500	0.79102100	H	-3.55400100	1.74732700	-0.64648100	C	-2.58037900	-1.68760100	0.05384600
H	-2.13973300	0.72799000	1.42794200	C	-3.19670200	-2.31563300	0.72814900	C	-3.02946300	0.56255000	-0.66842500
C	-0.72711500	3.57105200	-0.78999900	C	-5.80693500	0.79045800	-0.01241100	N	-5.57211900	-3.50589200	-0.54410100
H	0.74691800	2.13456100	-1.42922000	N	-6.40495200	1.78798700	-0.01503000	C	-1.21753600	-1.41347400	0.05341800
H	-3.23223900	2.94541200	1.41793100	C	-5.04759000	-0.43541400	-0.01684200	H	-2.92403200	-2.67661400	0.34218700
H	-0.32403600	4.36264400	-1.41648400	C	5.04750800	0.43544000	-0.01667000	C	-1.66683900	0.83423900	-0.66496700
C	-0.79599100	-1.17798800	-0.00167000	C	-5.73157300	-1.59546900	-0.06030300	H	-3.71724200	1.33222600	-1.00569400
C	-0.44430800	-2.27642600	0.79980000	H	-5.22414400	-2.55309400	-0.10281600	C	-0.72599500	-0.14529200	-0.30008200
C	-1.94739700	-1.26186000	-0.80154500	H	-6.81558800	-1.60868400	-0.06654200	H	-0.52362700	-2.19040700	0.36136300
C	-1.22297800	-3.43204100	0.79077800	C	5.73161200	1.59545000	-0.05958400	H	-1.32255000	1.81043900	-0.99417100
H	0.43985000	-2.21715300	1.42644300	H	6.81562400	1.60855100	-0.06591200	C	0.72599400	0.14527200	-0.30008400
C	-2.73028300	-2.41463400	-0.78901400	H	5.22432800	2.55317300	-0.10167100	C	1.21753500	1.41346100	0.05341600
C	-2.22422000	-0.42036400	-1.42939800				C	1.66683800	-0.83425200	-0.66497200	
C	-2.32721400	-3.50866500	0.00185900				C	2.58037900	1.68758800	0.05384100	
H	-0.93491300	-4.27200500	1.41769800				H	0.52362700	2.19039300	0.36136200	
H	-3.61800000	-2.46110600	-1.41457400				C	3.02946200	-0.56256200	-0.66843200	
C	1.41835000	-0.10052300	-0.00120800				H	1.32254800	-1.81045200	-0.99417500	
C	2.19338300	0.74942700	0.80475100				C	3.52015000	0.70092600	-0.29248700	
C	2.06722600	-1.05152100	-0.80562000				H	2.92403200	2.67660200	0.34218100	
C	3.58358900	0.65336100	0.79543200				H	3.71724100	-1.33223700	-1.00570400	
H	1.69968300	1.48246400	1.43479800				C	4.97636500	0.99367000	-0.26210000	
C	3.45708300	-1.15218300	-0.79402900				C	5.33120400	2.37229300	-0.42079200	
C	1.47642600	-1.70792400	-1.43660300				C	5.91680000	0.02156600	-0.06568200	
H	4.16657000	1.31982100	1.42592900				N	5.57211300	3.50588300	-0.54411300	
H	3.94143300	-1.89435600	-1.42341600				H	5.50784600	-0.96925600	0.12015500	
H	-2.98143700	-4.40835800	0.00327100				C	7.36805000	0.05419700	-0.03094600	
C	-1.85339200	3.80838700	0.00075800				C	8.03459000	-1.14067900	0.32163900	
H	-2.32890900	4.78504600	0.00109600				C	8.18049200	1.17204400	-0.32824200	
C	4.22539600	-0.29943800	0.00139200				C	9.41530300	-1.22504600	0.39238900	
H	5.30893700	-0.37626900	0.00248500				H	7.44408300	-2.02171600	0.56276600	
						C	9.56242200	1.09422600	-0.27075500		
						H	7.73162500	2.11112200	-0.62673800		
						C	10.21307600	-0.10280800	0.09474600		
						H	9.88540600	-2.15776300	0.68390300		
						H	10.15451800	1.96749100	-0.52158400		
						N	11.61627100	-0.17377500	0.15549800		
						C	12.39012500	0.97410000	0.50346800		
						C	12.29722500	-1.39547100	-0.12733400		
						C	12.03775400	1.76404300	1.60808900		
						C	13.52401400	1.31311600	-0.24922400		
						C	13.31870300	-1.84604300	0.72170700		
						C	11.96809800	-2.14880900	-1.26450900		
						C	12.80175200	2.88104000	1.94190300		
						H	11.16633900	1.49918900	2.19878600		
						H	14.29204100	2.42182400	0.10234300		
						C	13.79697600	0.70481200	-1.10583700		
						C	13.99914600	-3.02791400	0.43349400		
						H	13.57435500	-1.26532300	1.60245200		
						C	12.64217200	-3.33824700	-1.53565900		

Figure S6. SEM images of **VH-MON/TiO₂-Pt** composites before and after the five successive photocatalytic reactions.

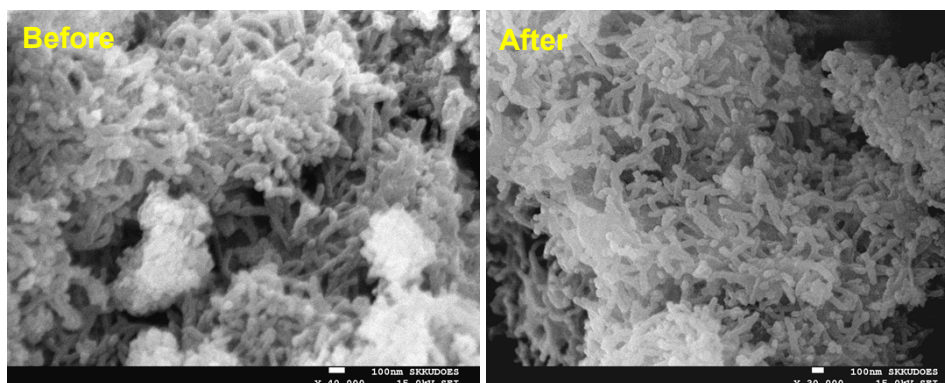


Figure S7. A plot of $(F(R)h\nu)^2$ versus photon energy ($h\nu$) using the reflectance spectrum of **VH-MON** (based on the Kubelka-Munk theory).

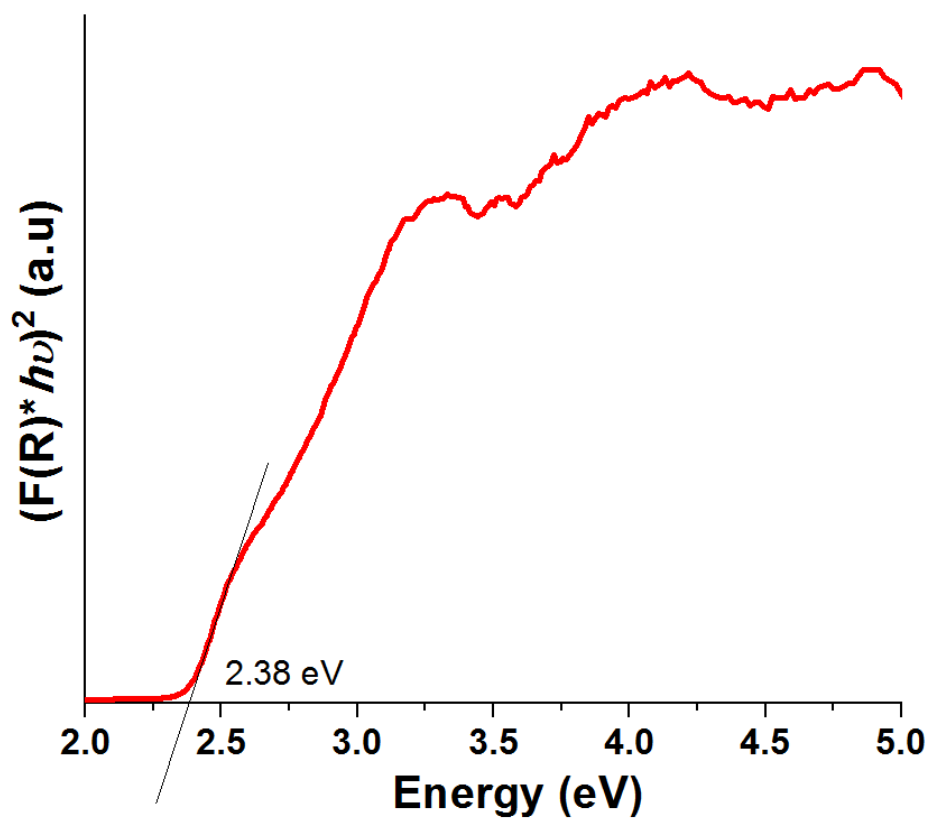
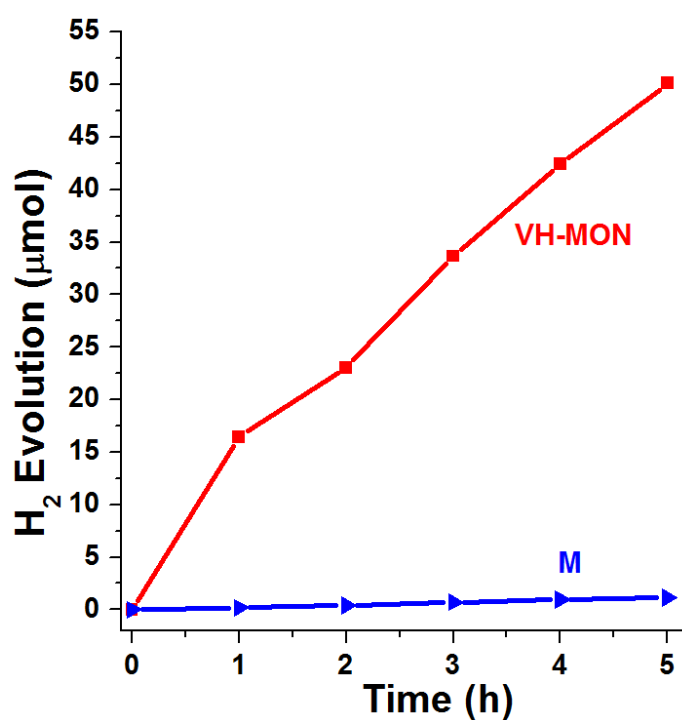
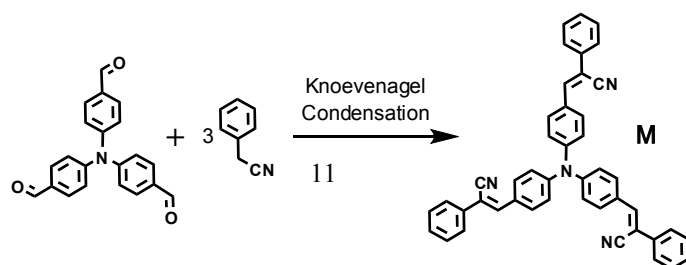


Figure S8. Visible light-induced hydrogen production from water using monomeric dye* (**M**, blue color) and **VH-MON** (red color).



*Experimental procedure for monomeric dye (**M**)



M is a known compound (ref. Tomoni, O., *Electrophotographic photosensitive materials*, Jpn. Kokai Tokkyo Koho JP07175236, **1995**). For synthesis of **M**, tri(4-formylphenyl)amine (1.0 mmol, 330 mg) and benzyl cyanide (3.3 mmol, 390 mg) were dissolved in THF (30 mL) in a 50 mL Schlenk flask,. To this solution, NaOH (3.0 mmol, 120 mg) in 10mL EtOH was added. The reaction mixture was heated at 70°C for 4 hours. The crude mixture was extracted with dichloromethane, and the organic layer was dried over MgSO₄ and then concentrated in vacuo. The residue was purified by silica gel column chromatography with n-hexane/EtOAc. HRMS (EI⁺) calc. for [C₄₅H₃₁N₄]⁺ 627.2549, found 627.2545. **M** (4 mg) and TiO₂-Pt (4 mg) were used in photocatalytic reaction. Other conditions were same with those for **VH-MON-TiO₂-Pt** composite. As shown below, after 5 hours, 1.1 μmol of hydrogen evolution was observed.

Table S2. External quantum efficiencies of photocatalytic systems.

run	Eosin-Y/TiO₂-Pt		N719/TiO₂-Pt		VH-MON/TiO₂-Pt	
	moles of H ₂ (mmol)	External QE ^a (%)	moles of H ₂ (mmol)	External QE ^a (%)	moles of H ₂ (mmol)	External QE ^a (%)
1	82	8.6	43	4.5	50	5.2
2	12	1.3	26	2.7	47	4.9
3	6	0.6	19	2.0	52	5.5
4	2	0.2	12	1.3	46	4.8
5	-	-	-	-	45	4.7

^aThe external quantum efficiencies (QE) were measured under same photocatalytic reaction conditions by comparison of the number of produced hydrogen molecules with the number of incident photons for 5 hours. The focused light intensity and area on the reaction tube (20 cm distance between light source and reaction tube) were 4.6 mW cm⁻² and 6 cm², respectively. The QEs were calculated using the following equations.

$$\frac{\text{Photons}}{\Delta t} = \frac{\text{Wattage of flux}}{h \cdot \nu}$$

$$\text{Quantum Efficiency}(\%) = \frac{2 \times \text{number of hydrogen (H}_2\text{) molecules}}{\text{number of incident photons}}$$

(*h*: planck constant, *ν*: frequency of light)