Supporting Information

Organic semiconductor for artificial photosynthesis: Water splitting into hydrogen by a bioinspired $C_3N_3S_3$ polymer under visible light irradiation

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Catalyst preparations

$Cd_3(C_3S_3N_3)_2$: 1.0 mmol of trithiocyanuric acid trisodium solution was dissolved in 100 ml of water, and then was dropped slowly into 1.5 mmol of $Cd(NO_3)_2$ solution (100 ml) with vigorously stirring at room temperature. After 24 h, the yellow $Cd_3(C_3S_3N_3)_2$ precipitate was filtered, washed several times with deionized water, and finally dried in vacuous at 60 °C.

Catalyst characterizations

The X–ray diffraction (XRD) measurements were performed on a Bruker D8 Advance X–ray diffractometer using Cu Kα1 radiation (λ=1.5406 Å). The surface morphologies of the polymer were observed using a field emission scanning electron microscope (FESEM: America, FEI Nova NanoSEM 230)

The XPS was carried out on an ESCALAB 250 XPS System with a monochromatized Al Ka X-ray sources (15kv 200W 500um pass energy = 20 eV). Cyclic voltammetry measurements were performed at a scan rate of 10 mV s^{-1} in the range −1.4/+2 V with a platinum foil counter electrode and an Ag/AgCl reference electrode. All experiments were carried out under ambient conditions.

< Table S1>

Table S1 Elemental Analysis of polymer

Element	N	C	S
Content (wt.%)	21.8	19.07	54.14
Molar ratio	**N : C : S = 1 : 1.02 : 1.08**		

<Figure S1>

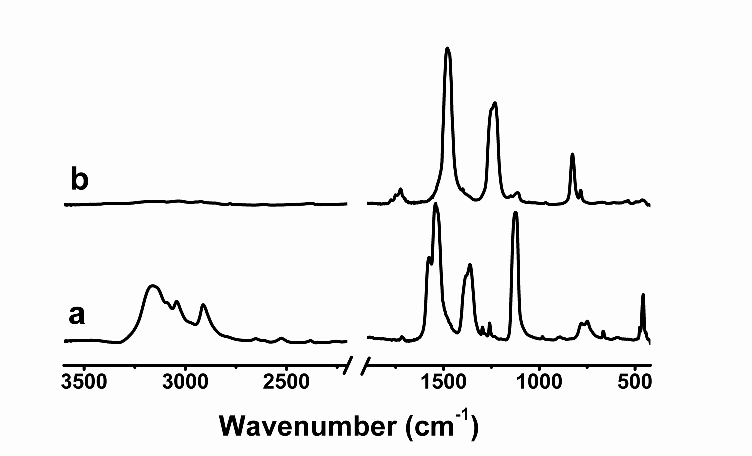


Figure S1 FTIR spectra of trithiocyanuric acid (a) and poly(trithiocyanuric acid) (b).

The IR spectrum of trithiocyanuric acid (a) is well consistent with that reported in literature [1, 2]. The major bands observed at 1540, 1125, and 750 cm^{-1} in the IR spectrum belong to the characteristic of the nonaromatic, thirthione form of the triazine ring. Specifically, 1125 cm^{-1} is assigned to C=S stretching vibrations. The peaks at the position of 2900 – 3160 cm^{-1} are attributed to -N-H stretching vibrations. After oxidative polymerization of trithiocyanuric acid (spectrum b), both of peaks at 2900 – 3160 and 1125 cm^{-1} disappear in the IR spectrum. On the other hand, the characteristic peaks around 1483, 1234, and 827 cm^{-1} of the aromatic, trithiol form of the ring appear, as found in the spectrum of tri (S-methyl) trithiocyanurate [3]. This indicates that poly(trithiocyanuric acid) is successfully synthesized, as anticipated.

[1] G. A. Loughran, G. F. L.Ehlers, W. J. Crawford, J. L. Burkett, J. D. Ray, *Appl. Spectr.* **1964**, 18, 129.

[2] A. Mieczys, E. C. Kucharski, *J. Appl Poly. Sci.* **2000**, 76, 439.

[3] R. Kevin, A. R. Henke, M. K. Hutchison, S. P. D. A. A. Krepps, *Inorg. Chem.* **2001,** 40*,* 4443.

<Figure S2>

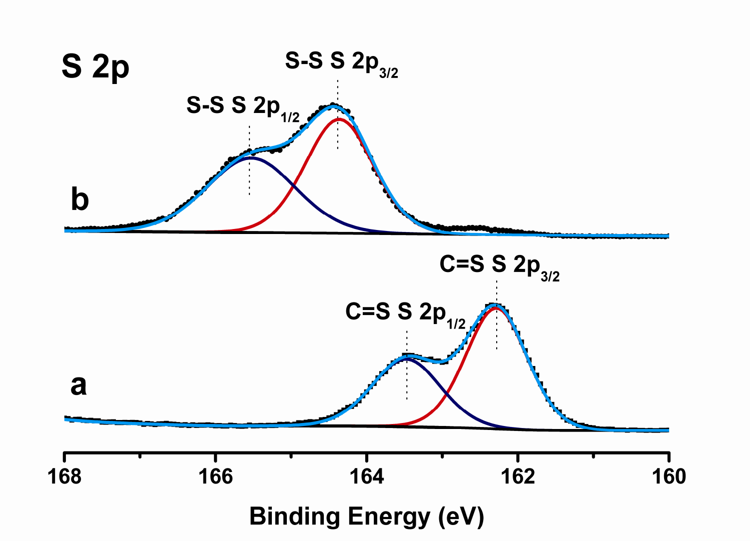


Figure S2 XPS for S 2p of trithiocyanuric acid (a) and poly(trithiocyanuric acid) (b).

The S 2p XPS spectrum (line a) of trithiocyanuric acid has a S 2p$_{3/2}$ binding energy of 162.3 eV, a 1:2 relative intensity, a 1.2 eV peak difference between S 2p$_{1/2}$ and S 2p$_{3/2}$, the same as the spectrum of C=S bond in 6-Dibutylamino-1,3,5-triazine-2,4-dithiol. [4] Upon oxidative polymerization of trithiocyanuric acid, the binding energy of S 2p$_{3/2}$ and S 2p$_{1/2}$ shifts to 164.4 and 165.6 eV (line b), respectively, which is attributed to S-S bonds. [4] This also indicates that poly(trithiocyanuric acid) is successfully synthesized as anticipated.

[4] M. Kunio, K. Suzuki, K. Shimizu, Y. Oishi, *Langmuir* **2002**, 18, 9527.

<Figure S3>

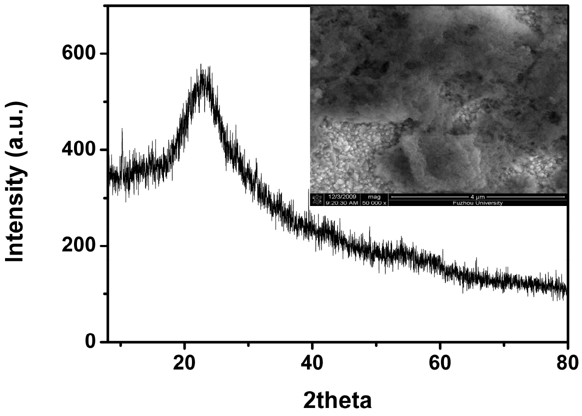


Figure S3 XRD and SEM (insert) patterns of the as-prepared $C_3N_3S_3$ polymer

<Figure S4>

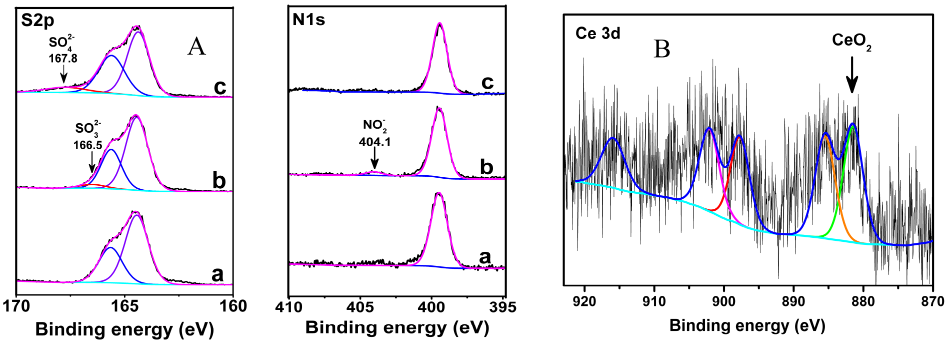


Figure S4 A) S2p and N1s XPS spectra of the bare $C_3N_3S_3$ polymer (a), the $C_3N_3S_3$ polymer without a sacrificial agent after reaction for 48 h under $\lambda \geq 420$ nm light illumination (b), and the $C_3N_3S_3$ polymer in 2 mmol L^{-1} $Ce(SO_4)_2/Ce_2(SO_4)_3$ solution after reaction for 72 h (c). B) Ce 3d XPS spectra of the $C_3N_3S_3$ catalyst in 2 mmol L^{-1} $Ce(SO_4)_2/Ce_2(SO_4)_3$ solution after reaction for 72 h.

<Figure S5>

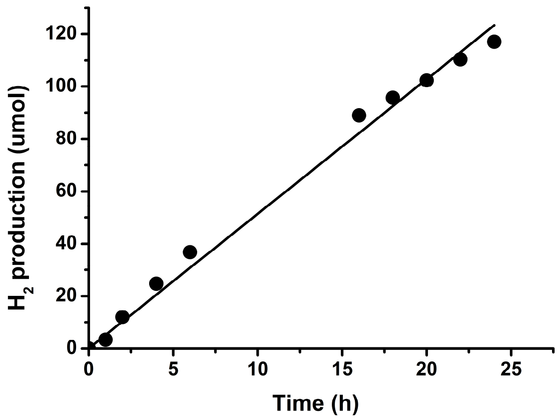


Figure S5 Time courses of H_2 evolution from pure water on single-wall carbon nanotube loaded polymer. Single-wall carbon nanotube loading is 5 wt.%. Experimental conditions: catalyst weight, 0.4 g; light wavelength, $\lambda \geq 420$ nm.

<Figure S6>

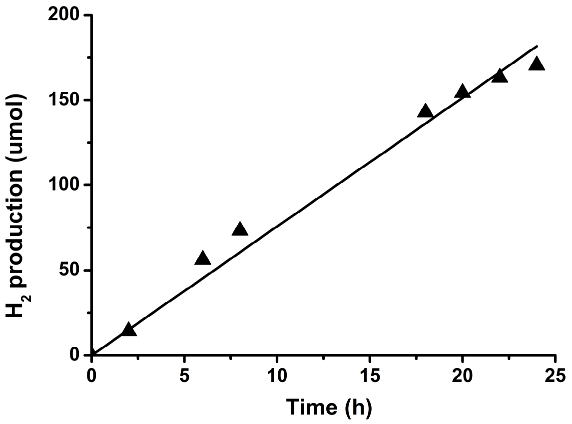


Figure S6 Time courses of H_2 evolution from water containing thiocyanate as a sacrificial electron donor on Ru loaded polymer. Ru loading is 3.0 wt.%. Experimental conditions: catalyst weight, 0.4 g; light wavelength, $\lambda \geq 420$ nm.

<Figure S7>

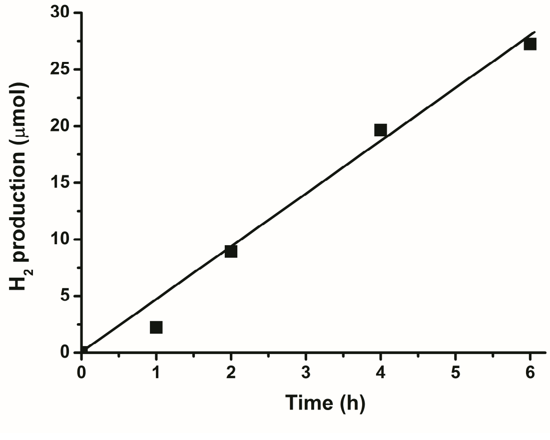


Figure S7 Time courses of H_2 evolution from pure water over $Cd_3(C_3N_3S_3)_2$ catalyst under $\lambda \geq 420$ nm light. Catalyst weight is 0.4 g

<Figure S8>

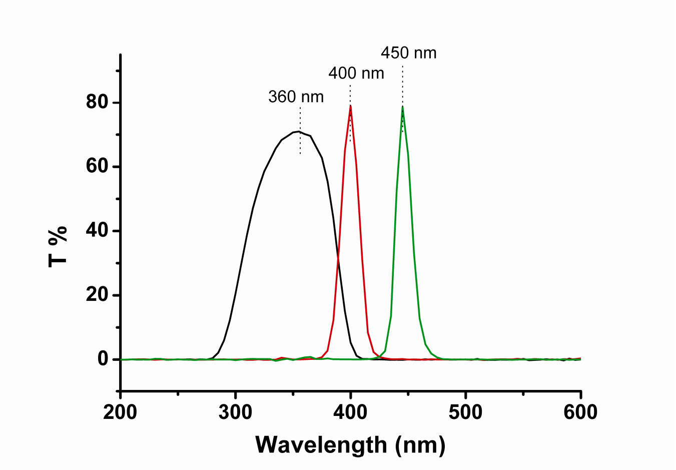


Figure S8 Spectral distributions of the band-pass filters

Description of Density Functional Theory Calculations (DFT)

The calculations were performed using the spin-unrestricted Kohn-Sham method with the Dmol^3 software package [5, 6]. The exchange-correlation functional was the generalized gradient approximation (GGA) of PW91. [7] In the Dmol^3 software, the physical wave functions are expanded in terms of accurate numerical basis sets. In this paper, we use the triple numerical plus polarization basis set (TNP). The use of numerical basis sets minimizes the basis set super position error (BSSE). [8] All atoms were treated with all-electron basis set. The tolerances of energy, gradient, and displacement convergence were 1×10^{-5} Hartree, 2×10^{-3} Hartree/Å and 5×10^{-3} Å, respectively.

[5] B. Delley, *J. Chem. Phys.* **1990**, 92, 508.

[6] B. Delley, *J. Chem. Phys.* **2000**, 113, 7756.

[7] J. P.Perdew, Y. Wang, *Phys. Rev. B* **1992**, 45, 13244.

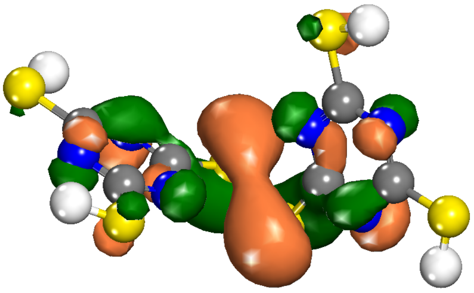
[8] N. Matsuzawa, J. Seto, D. A. Dixon, *J. Phys. Chem. A* **1997**, 101, 9391.

<Table S2>

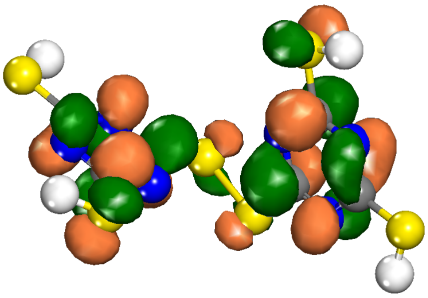
Table S2 Calculated HOMO and LUMO orbital energy of triazine monomers 2, 4, and 6.

Monomer number	2	4	6
HOMO/Ha	-0.2353	-0.2154	-0.2181
LUMO/Ha	-0.0968	-0.1048	-0.1140
Band gap/eV	3.77	3.01	2.83

(1)HOMO and LUMO orbital diagrams of triazine dimer

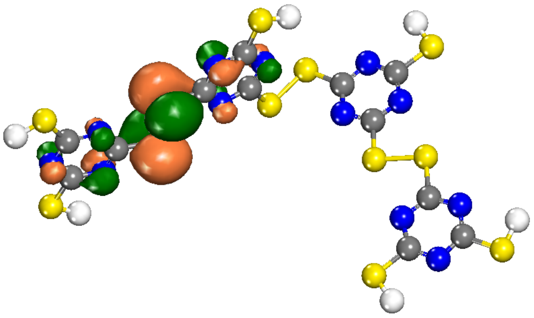


HOMO

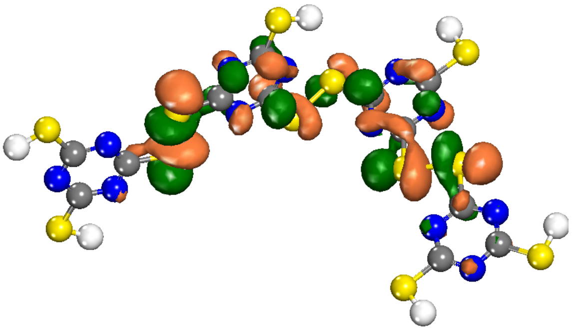


LUMO

(2) HOMO and LUMO orbital diagrams of triazine tetramer

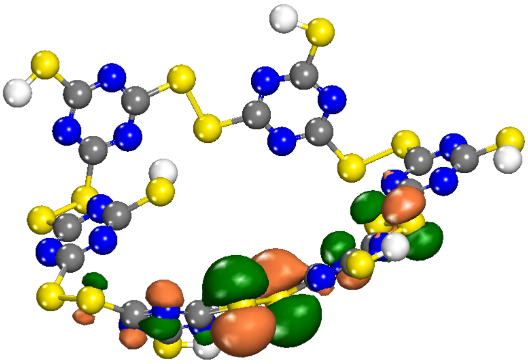


HOMO

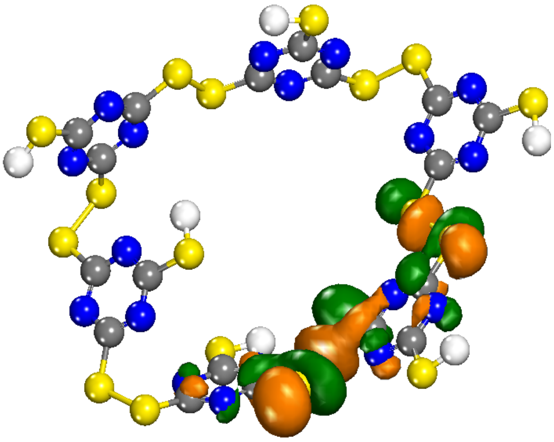


LUMO

(3) HOMO and LUMO orbital diagrams of triazine hexamer



HOMO



LUMO