

**Sustainable method toward melamine-based conjugated polymer semiconductors
for efficient photocatalytic hydrogen production under visible light**

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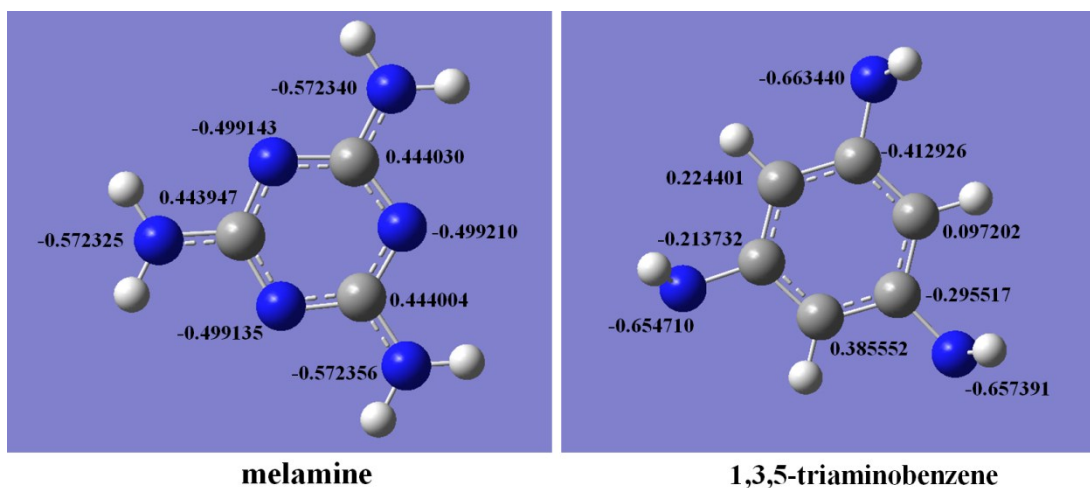


Figure S1. Electron density of melamine and 1,3,5-triaminobenzene calculated through Gauss.

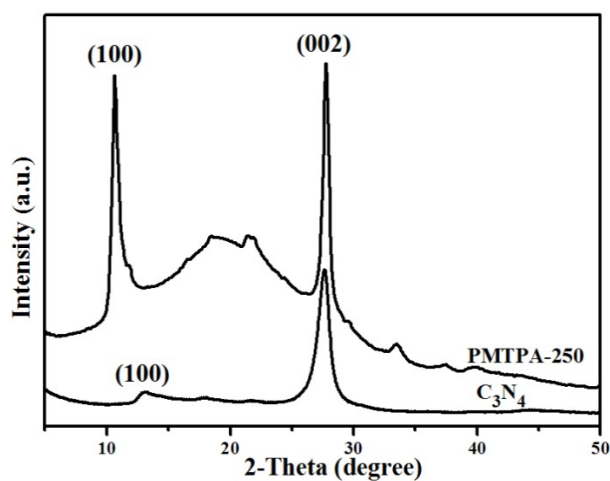


Figure S2. XRD patterns of C_3N_4 and PMTPA-250.

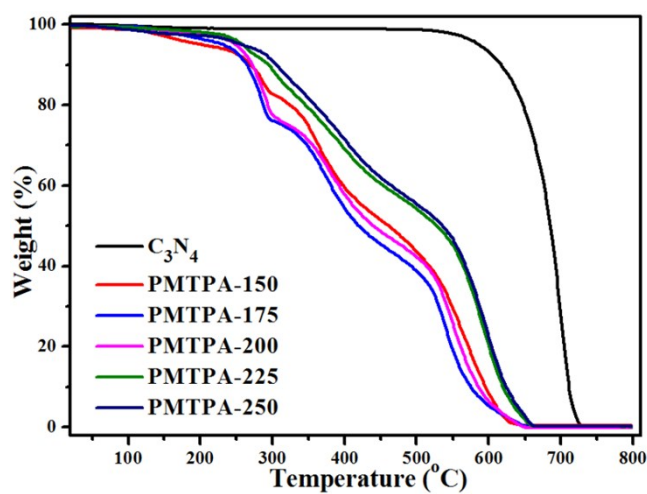


Figure S3. TGA curves of as-prepared samples with 10 °C/min increasing rate from room temperature to 800 °C.

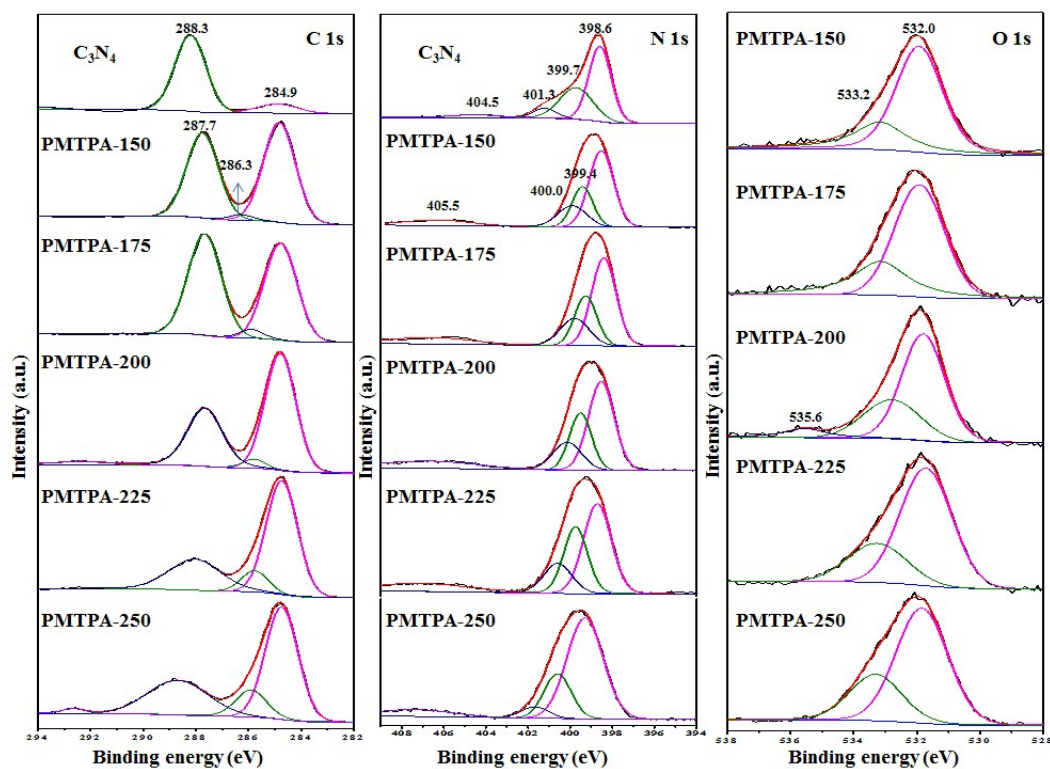


Figure S4. C 1s, N 1s and O 1s XPS spectra of the as-prepared samples.

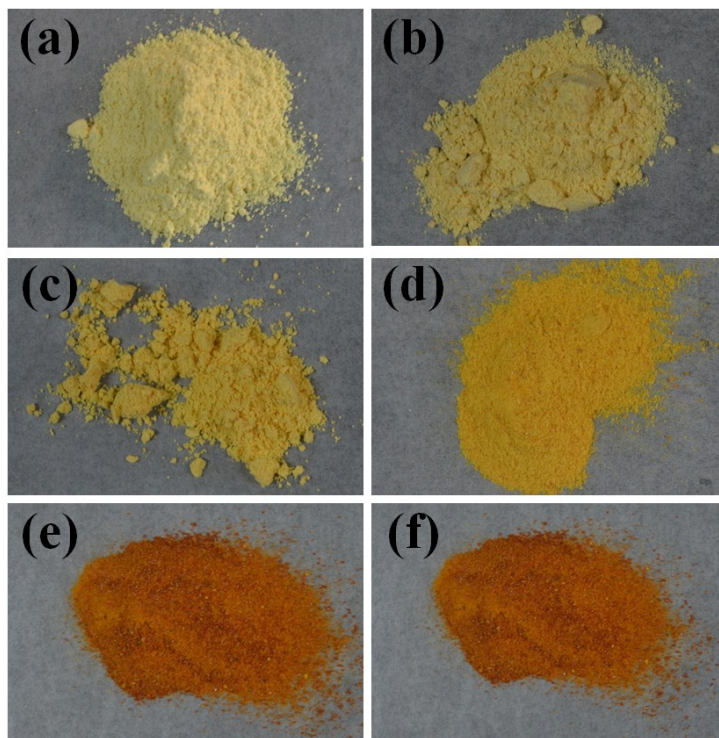


Figure S5. Sample pictures: (a) C₃N₄, (b) PMTPA-150, (c) PMTPA-175, (d) PMTPA-200, (e) PMTPA-225, (f) PMTPA-250.

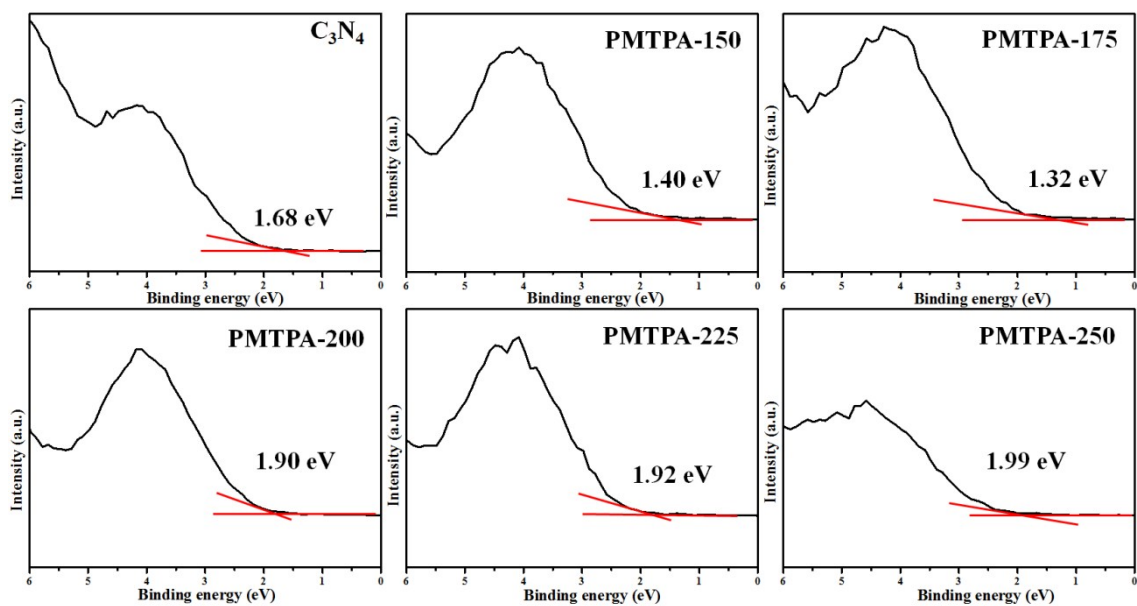


Figure S6. High-resolution valence band XPS spectra of as-prepared samples.

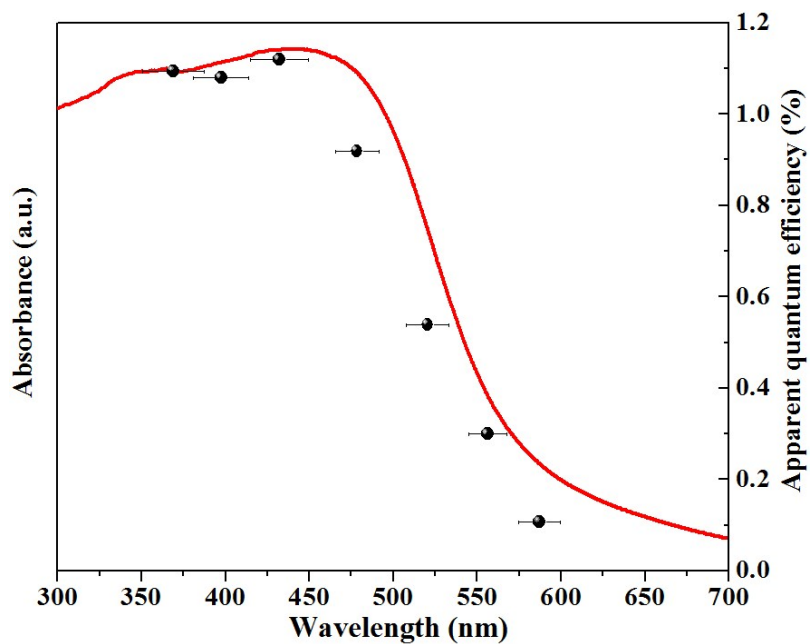


Figure S7. UV-Vis spectrum and AQE for PMTPA-250.

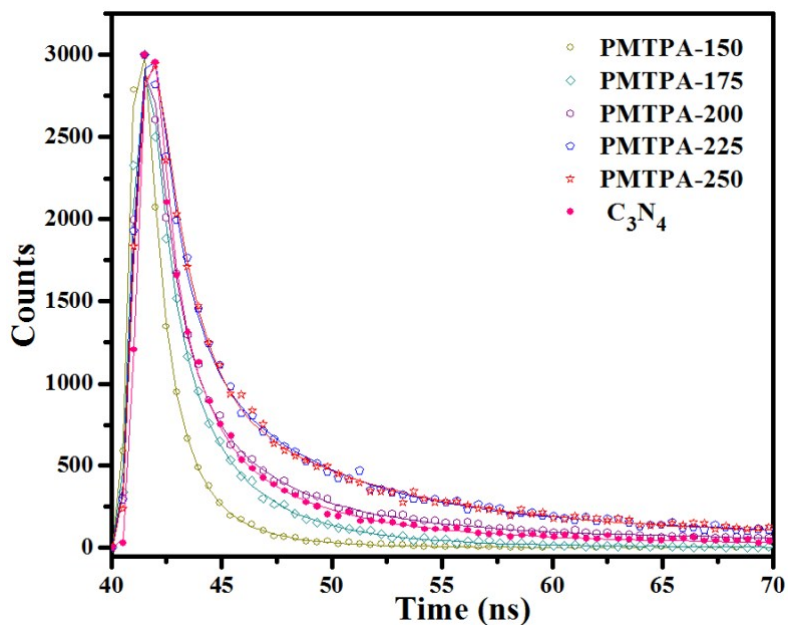


Figure S8. Time-resolved fluorescence decay spectra of PMTPA-150, PMTPA-175, PMTPA-200, PMTPA-225, PMTPA-250 and C₃N₄ samples monitored at 463, 523, 540, 558, 558 and 460 nm, respectively, by time-correlated single-photo counting. The samples were excited by the incident light of 340 nm.

Table S1. Physicochemical properties, band gap and VB/CB positions of as-prepared samples. VB was determined by high-resolution valence band XPS spectra, band gap was calculated from UV-Vis spectrum.

Sample	Surface area [m ² /g]	Band gap [eV]	VB/CB [eV]
C ₃ N ₄	14.3	2.78	1.68/-1.10
PMTPA-150	1.5	2.74	1.40/-1.34
PMTPA-175	2.0	2.62	1.32/-1.30
PMTPA-200	1.3	2.35	1.90/-0.45
PMTPA-225	1.3	2.21	1.92/-0.29
PMTPA-250	3.3	2.12	1.99/-0.13

Table S2. The fitting results of the fluorescence decay curves through a tri-exponential function.

Sample	τ_1 [ns]-Rel%	τ_2 [ns]-Rel%	τ_3 [ns]-Rel%	T _{average} [ns]
C ₃ N ₄	1.545-89.50%	8.402-9.80%	51.968-0.70%	10.06
PMTPA-150	0.2846-77.26%	1.2758-19.95%	3.6028-2.80%	1.307
PMTPA-175	0.5738-71.54%	2.3307-22.03%	5.2783-6.42%	2.5523
PMTPA-200	0.7377-78.10%	3.8828-19.25%	23.4117-2.64%	9.2074
PMTPA-225	0.9171-74.56%	5.5543-21.80%	32.9125-3.60%	15.1014
PMTPA-250	1.1792-78.13%	7.1488-19.08%	42.8416-2.78%	17.8619