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NH-rich red poly(heptazine imide) nanoparticle with simultaneously promoted exciton dissociation and activated n→π* electronic transition for boosted photocatalytic H_2 generation

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1 Experimental Section

To explore the origin of red, several reference samples were synthesized as follows:

(1) Melamine (2 g) and NaCl (6 g) or RbCl (6 g) were thoroughly ground with KSCN (1 g), and the mixture was calcined according to the heating procedure of RPHIx NP. The final samples were denoted as RPHI-NaCl and RPHI-RbCl, respectively.

(2) Melamine (2 g) and KCl (6 g) were thoroughly ground with NaSCN (1 g), and the mixture was calcined according to the heating procedure of RPHIx NP. The final samples were denoted as RPHI-NaSCN.

(3) KCl (6 g) and KSCN (1 g) were heated with the same calcining procedure as RPHIx NP, and the final sample color was white (Fig. S7).

(4) Melamine (2 g) and KSCN (1 g) were calcined with the same procedure as RPHIx NP, and the aqueous solution of obtained sample was reddish brown, while the sample was hardly available after washing (Fig. S8).

Table S1 The parameters for apparent quantum efficiency (AQE) calculation

Parameter	Description	Data
M	Mole number of H_2 evolution	Determined in the test (mol)
N_A	Avogadro constant	6.022×10^{23} mol^{-1}
h	Planck constant	6.626×10^{-34} J s
c	Speed of light	3×10^{8} m s^{-1}
P	Power of lamp	23.5 mW cm^{-2}
S	Irradiated area	38.465 cm^2
t	Reaction time	Determined in the test (s)
λ	Wavelength of monochromatic light	Determined in the test

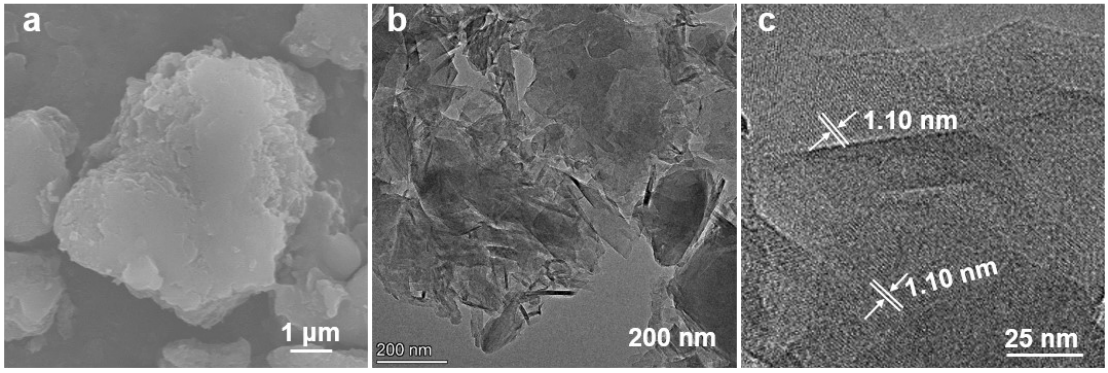

Fig. S1 (a) SEM; (b) TEM and (c) HRTEM images of PHI.

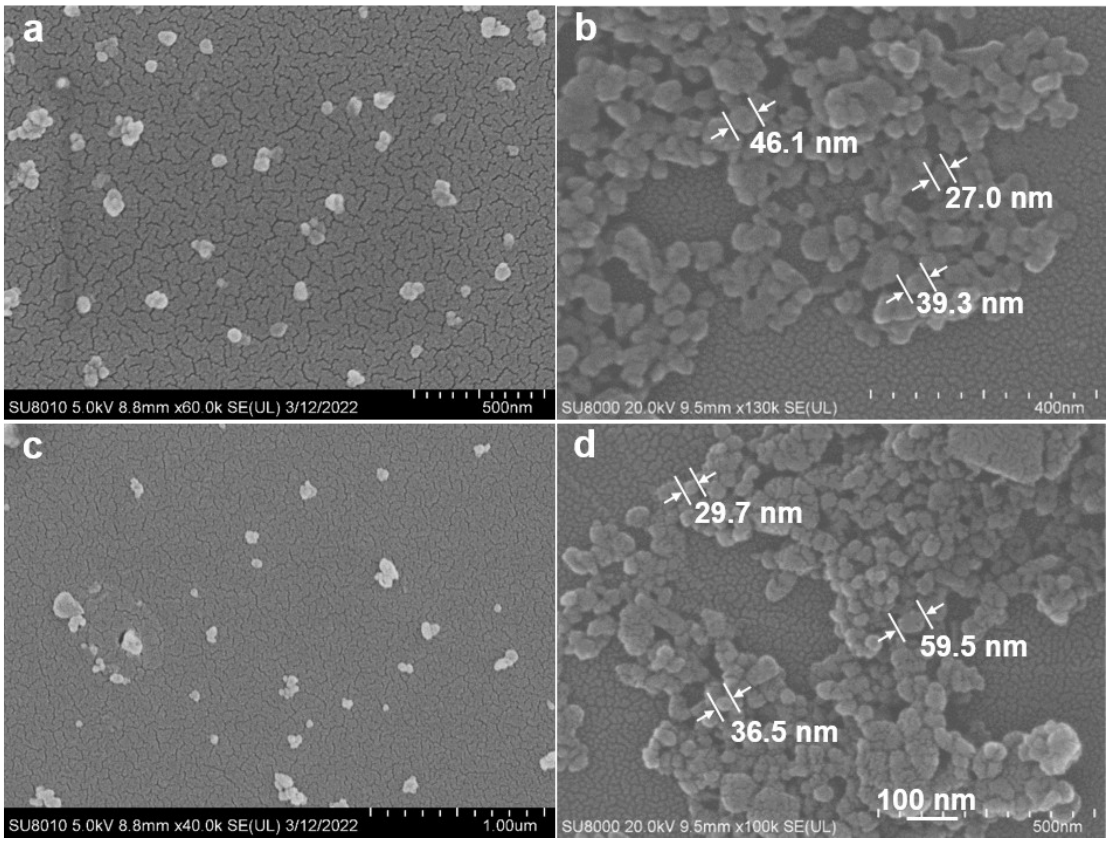

Fig. S2 SEM images of (a) (in ethanol) and (b) of RPHI0.75 NP; (c) (in ethanol) and (d) of RPHI1.1 NP.

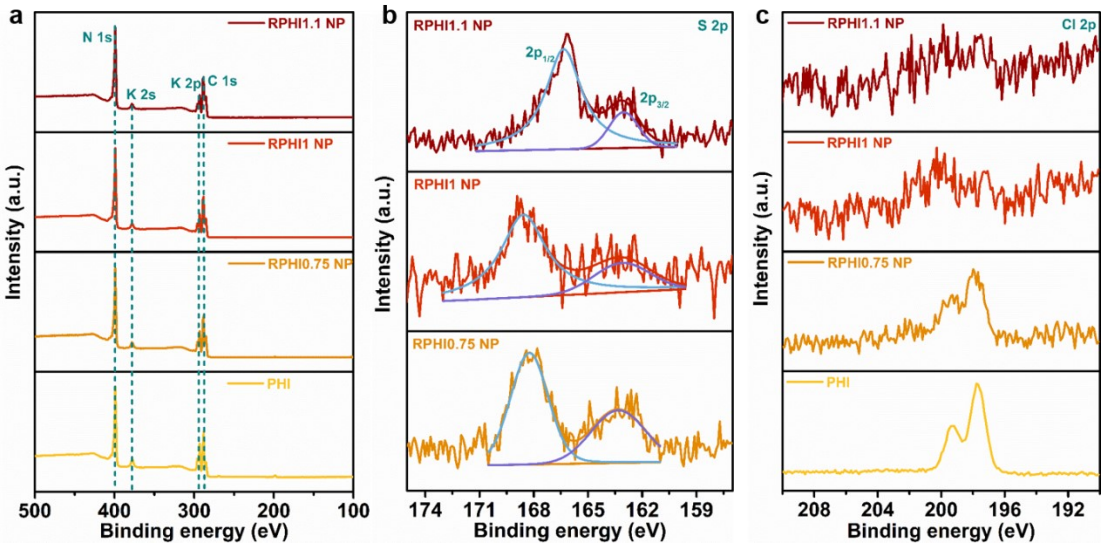

Fig. S3 XPS spectra of PHI and RPHIx NP: (a) Survey; (b) S 2p; (c) Cl 2p.

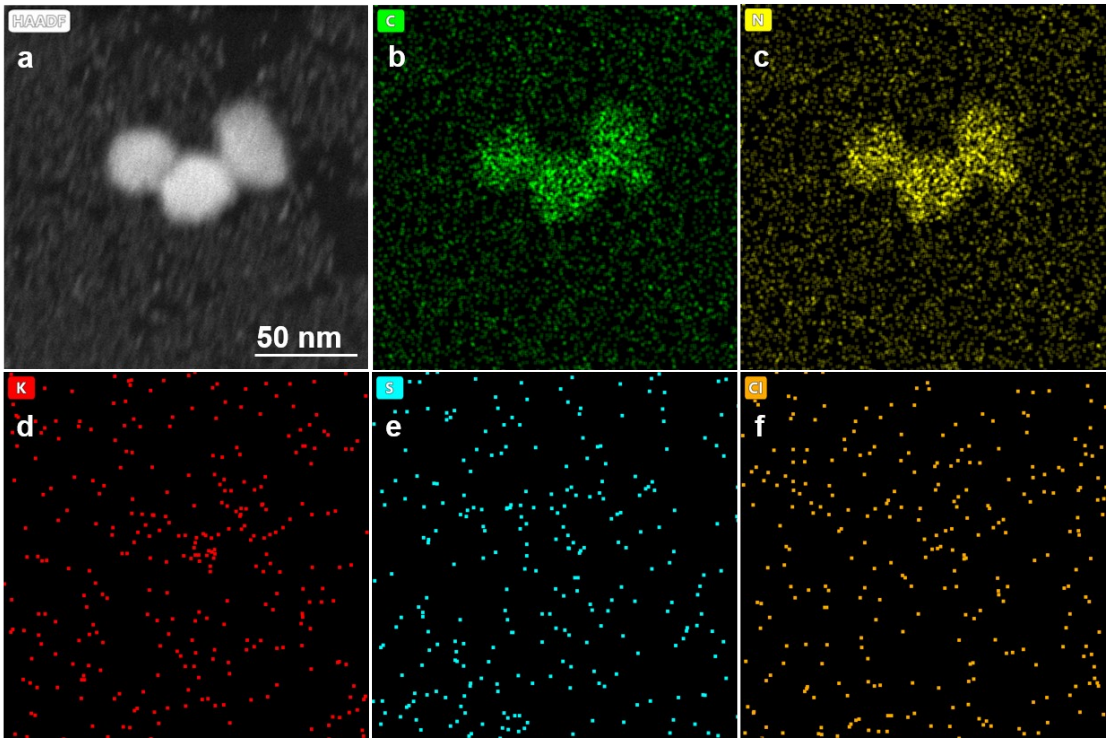

Fig. S4 EDS mapping of RPHI1 NP.

Table S2 The contents of C, N, K, O, Cl and S in PHI and RPHIx NP measured by XPS.

Samples	C (at%)	N (at%)	K (at%)	Cl (at%)	S (at%)	C/N (%)
PHI	42.15	47.11	5.08	0.45	–	89.5
RPHI0.75 NP	40.05	49.46	4.26	0.1	0.08	81.0
RPHI1 NP	39.83	50.37	3.84	0.04	0.05	78.8
RPHI1.1 NP	39.96	51.3	3.63	0.04	0.09	77.9

Table S3 Area ratio of deconvoluted peaks of ^{13}C NMR in Fig. 3a for PHI and RPHIx NP.

	$C\text{-}N_2\text{-}(NH_x)$ (C2)	$C\text{-}N_3$ (C3)	C2/C3
PHI	0.015	0.011	1.36
RPHI0.75 NP	0.006	0.004	1.5
RPHI1 NP	0.007	0.005	1.4
RPHI1.1 NP	0.008	0.004	2.0

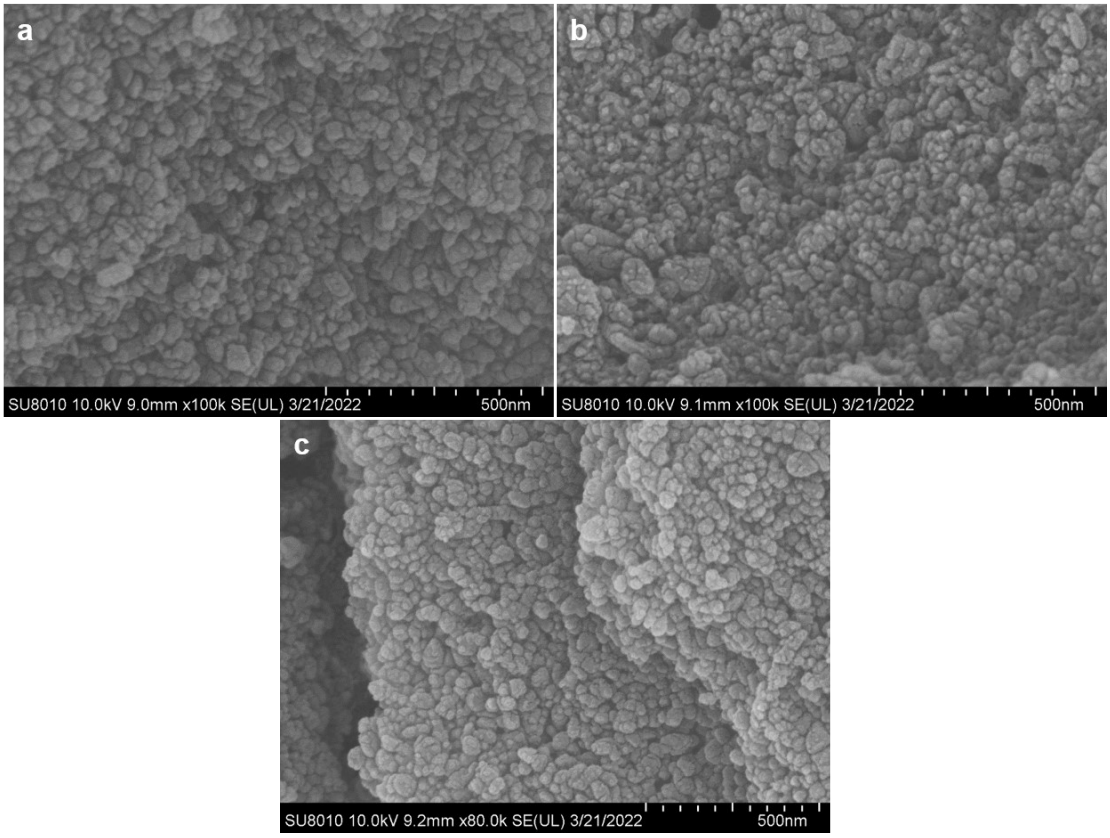

Fig. S5 SEM images of (a) RPHI-NaCl; (b) RPHI-RbCl and (c) RPHI-NaSCN.

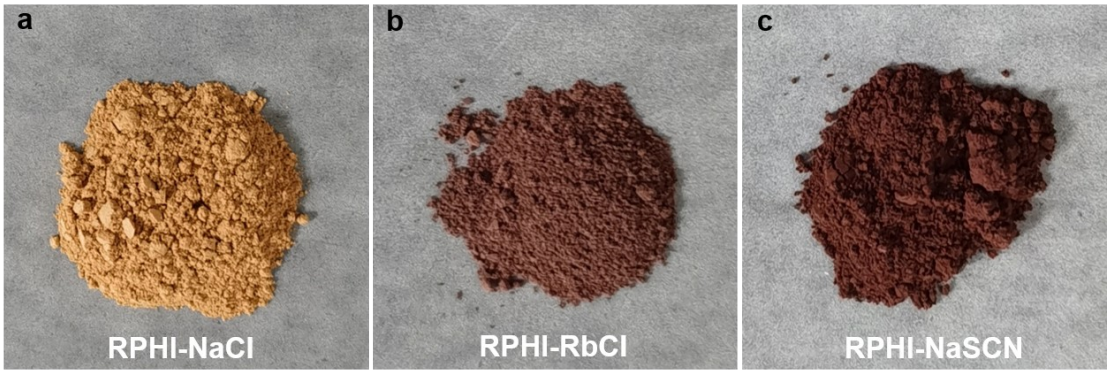

Fig. S6 The optical image of (a) RPHI-NaCl; (b) RPHI-RbCl and (c) RPHI-NaSCN.

Fig. S7 Images of calcined products of KCl and KSCN: (a) after cooling; (b) and (c) after dissolving in water.

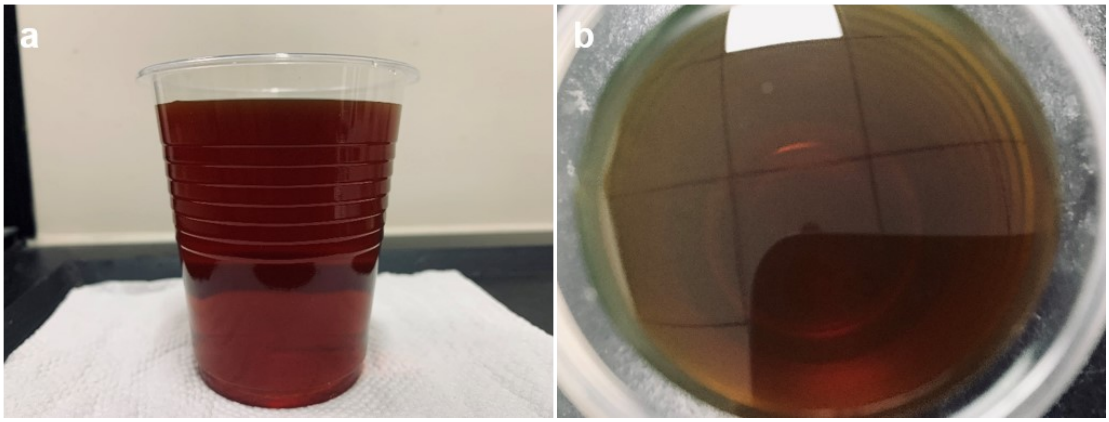

Fig. S8 Images of calcined products of melamine and KSCN dissolved in water.

Table S4 Fluorescence lifetimes and their percentages of photo-induced carriers in PHI and RPHIx NP.

Samples	τ_1/ns	A_1/%	τ_2/ns	A_2/%	τ_3/ns	A_3/%	τ/ns
PHI	5.04	70.64	38.68	29.36	—	—	14.92
RPHI0.75 NP	0.57	73.37	3.22	23.38	22.0	3.24	1.88
RPHI1 NP	0.59	72.28	3.07	24.04	16.9	3.68	1.79
RPHI1.1 NP	0.62	76.56	3.33	20.40	33.74	3.04	2.18

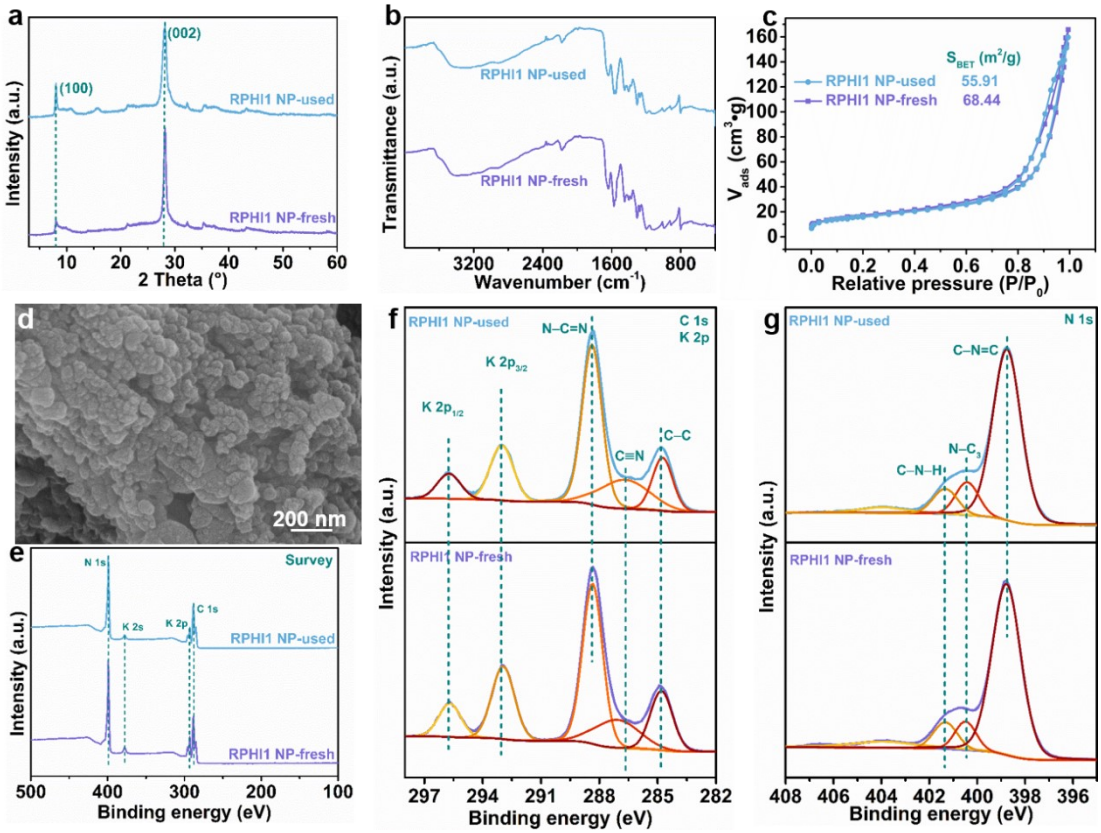

Fig. S9 (a) XRD patterns; (b) FTIR spectra; (c) N_2 absorption-desorption isotherm curves of RPHI1 NP before and after H_2 evolution; (d) SEM image of RPHI1 NP after H_2 evolution; XPS spectra of (e) Survey; (f) C 1s and K 2p; (g) N 1s of RPHI1 NP before and after H_2 evolution.

Table S5 HER comparison of RPHI1 NP with previously reported red PHI.

Photocatalyst	Light source	Sacrificial agent (vol%)	HER rate (μmol g^{-1} h^{-1})	
			λ > 420 nm	λ > 510 nm
OKCN2 [1]	300 W Xe lamp	20% TEOA	214.3	46.1
KCN [1]	300 W Xe lamp	20% TEOA	392.2	4.1
RPCN [2]	300 W Xe lamp	10% TEOA	1400	640
kPCN [2]	300 W Xe lamp	10% TEOA	< RPCN	—
CN-OA-M [3]	LED light	10% TEOA	168 white light	17 green light
CN-M [3]	LED light	10% TEOA	300 white light	0.45 green light
TKCN(0.2) [4]	300 W Xe lamp	20% TEOA	523.8	46.7
KCN [4]	300 W Xe lamp	20% TEOA	394.3	4.4
CN-OA-0.03 [5]	green LED light	10% TEOA	—	4
RPHI1 NP [This work]	300 W Xe lamp	10% TEOA	1292	297
PHI [This work]	300 W Xe lamp	10% TEOA	1109	12

Reference

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