Supplementary Information

Non-Photochromic Solar Energy Storage in Carbon Nitride Surpassing Blue Radicals for Hydrogen Production

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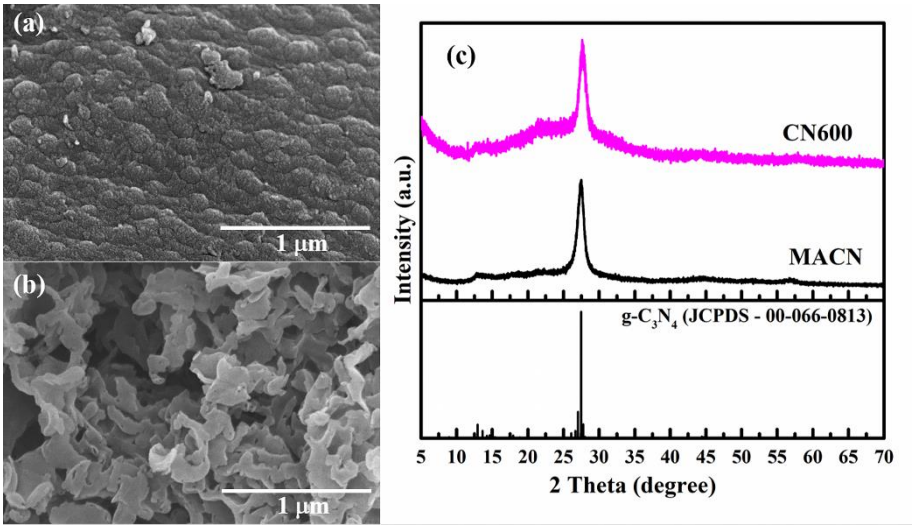

Fig. S1. SEM images of (a) MACN and (b) CN600. (c) XRD patterns of MACN and CN600.

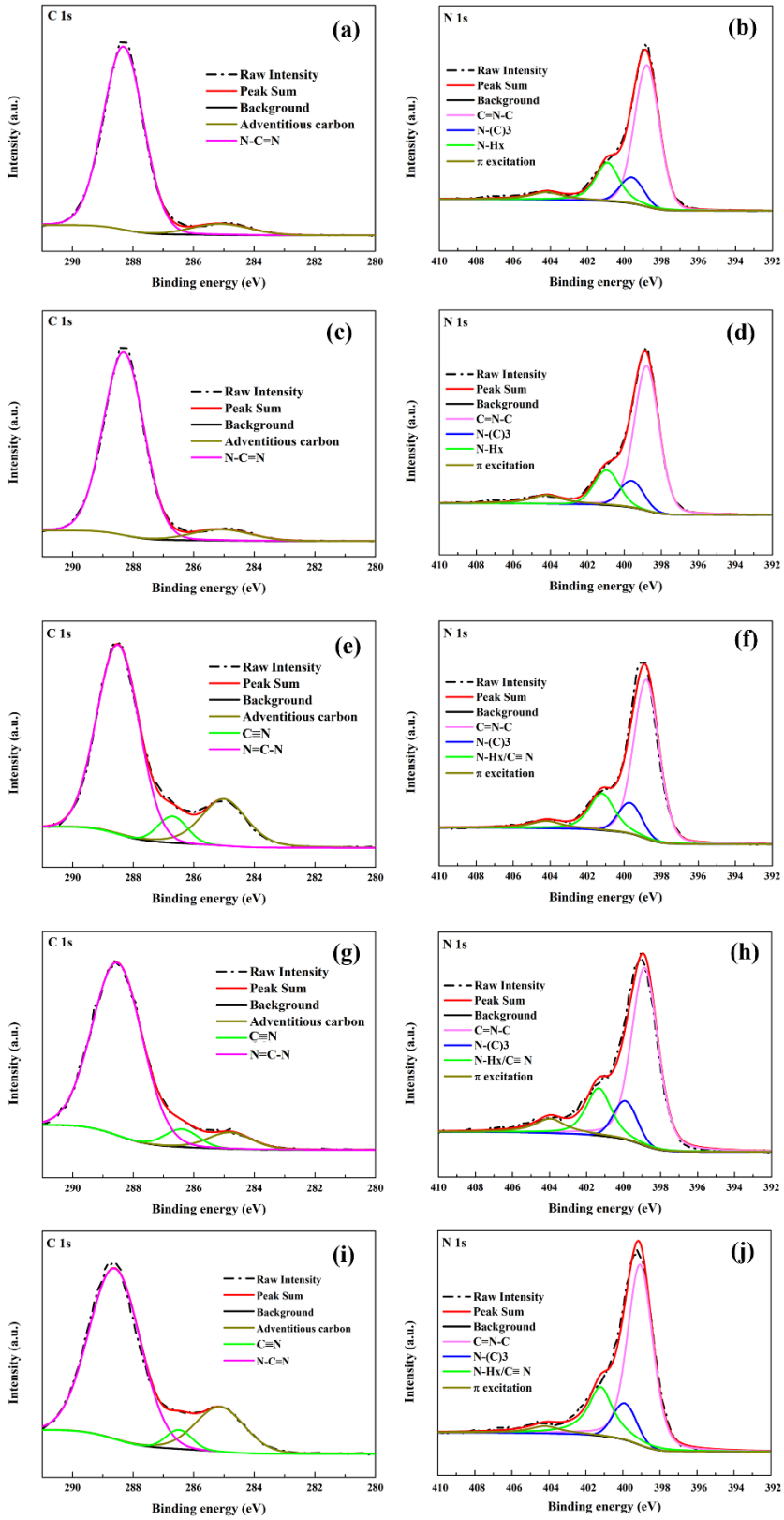

Fig. S2. C 1s and N 1s XPS spectra of (a),(b) MACN; (c),(d) CN600; (e),(f) KMACN400; (g),(h) KMACN400; and (i),(j) KCN, respectively.

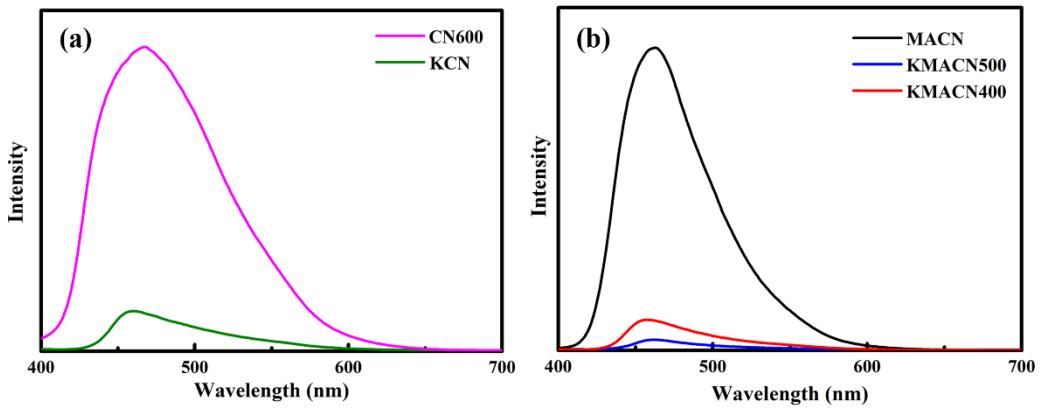

Fig. S3. PL spectra of (a) CN600 and KCN as well as (b) MACN, KMACN400, and KMACN500.

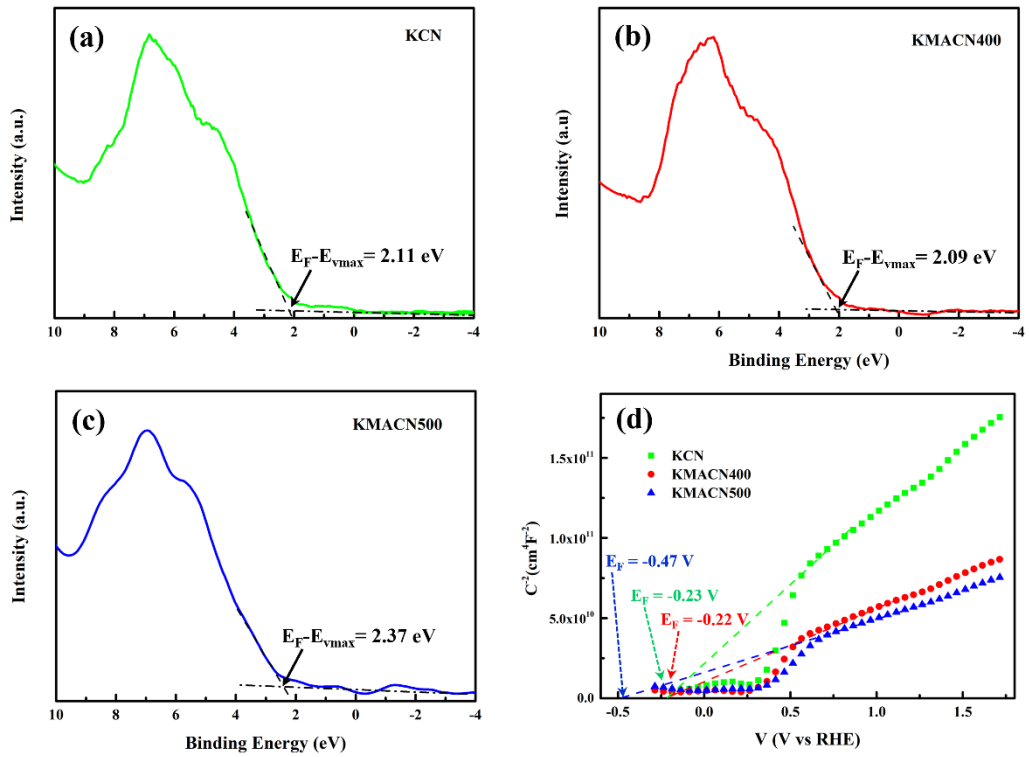

Fig. S4. XPS valance band spectra of (a) KCN, (b) KMACN400, and (c) KMACN500. (d) Mott-Schottky plots of the three KPHIs.

Calculation of AQY

The AQY values shown in Fig. 5c are calculated based on the following eqs (S1)-(S3). The measured monochromatic light power densities and hydrogen production rates (using KMACN500 as an example) under monochromatic light irradiation for AQY calculation are listed in Table S1.

$$AQY(\lambda)(\%) = \{[No.of\ electrons(\lambda)/sec]/[No.of\ photons(\lambda)/sec]\} \times 100\% \quad \text{(S1)}$$

$$No.of\ photons(\lambda)/sec = \{monochromatic\ light\ power\ density(\lambda)\ (W/cm^2) \times irradiated\ area\ (cm^2) \times \frac{1\left[\frac{(J/sec)}{W}\right]}{1.6\times10^{-19}\left(\frac{J}{eV}\right)\times\left[\frac{energy(\lambda)\ (eV)}{photon}\right]}\} \quad \text{(S2)}$$

$$No.of\ electrons(\lambda)/sec = H_2\ production\ rate(\lambda)\left(\frac{mol}{sec}\right)\times 2\left(\frac{mol\ of\ electrons}{mol\ of\ H_2}\right)\times 6\times10^{23}\left(\frac{no.of\ electrons}{mol\ of\ electrons}\right) \quad \text{(S3)}$$

Table S1. Monochromatic light power densities, hydrogen production rates under monochromatic light irradiation, and calculated AQYs for KMACN500. (Irradiated area = 9.375 cm^2)

Wavelength/Energy of monochromatic light (nm/eV)	Power density (W/cm^2)	No. of photon/sec	H_2 production rate (mol/s)	No. of electron/sec	AQY(%)
600/2.07	7.49×10^{-4}	2.12×10^{16}	1.94×10^{-12}	2.36×10^{12}	0.011
550/2.25	6.77×10^{-4}	1.76×10^{16}	3.89×10^{-13}	4.59×10^{11}	0.003
500/2.48	6.10×10^{-4}	1.44×10^{16}	7.08×10^{-12}	8.52×10^{12}	0.059
450/2.76	5.09×10^{-4}	1.08×10^{16}	2.79×10^{-10}	3.36×10^{14}	3.1
400/3.1	1.97×10^{-4}	3.73×10^{15}	4.86×10^{-10}	5.85×10^{14}	15.7

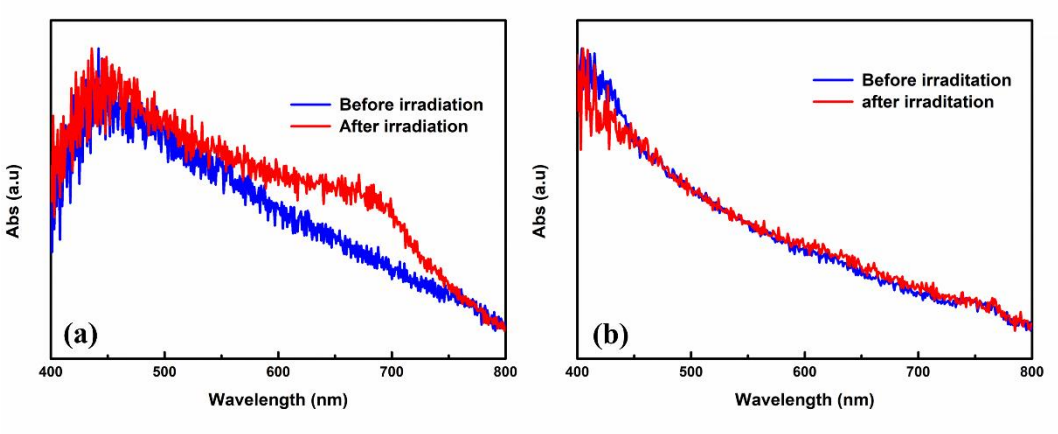

Fig. S5. Absorption spectra of (a) KMACN500 and (b) KCN solutions before and after irradiation.

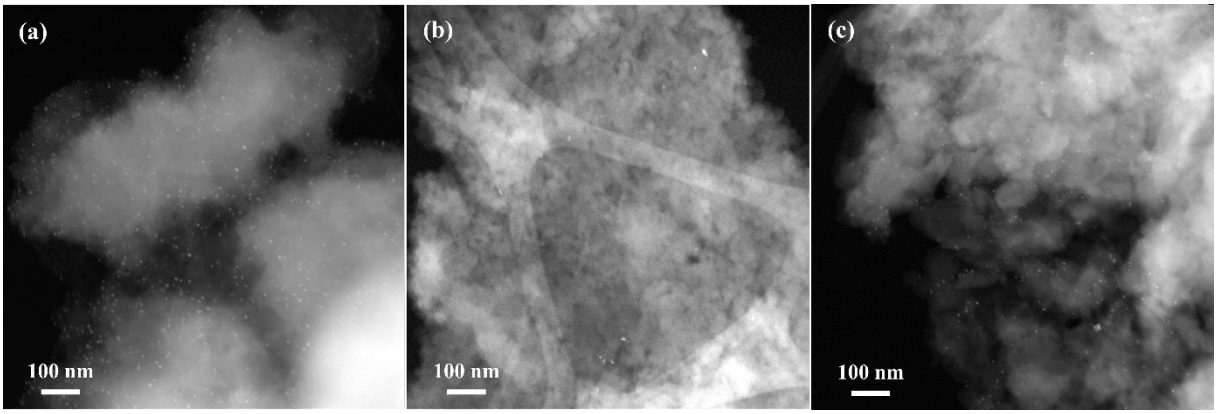

Fig. S6. HAADF STEM images of (a) KCN, (b) KMACN500, and (c) KAMCN400 after dark photocatalysis.

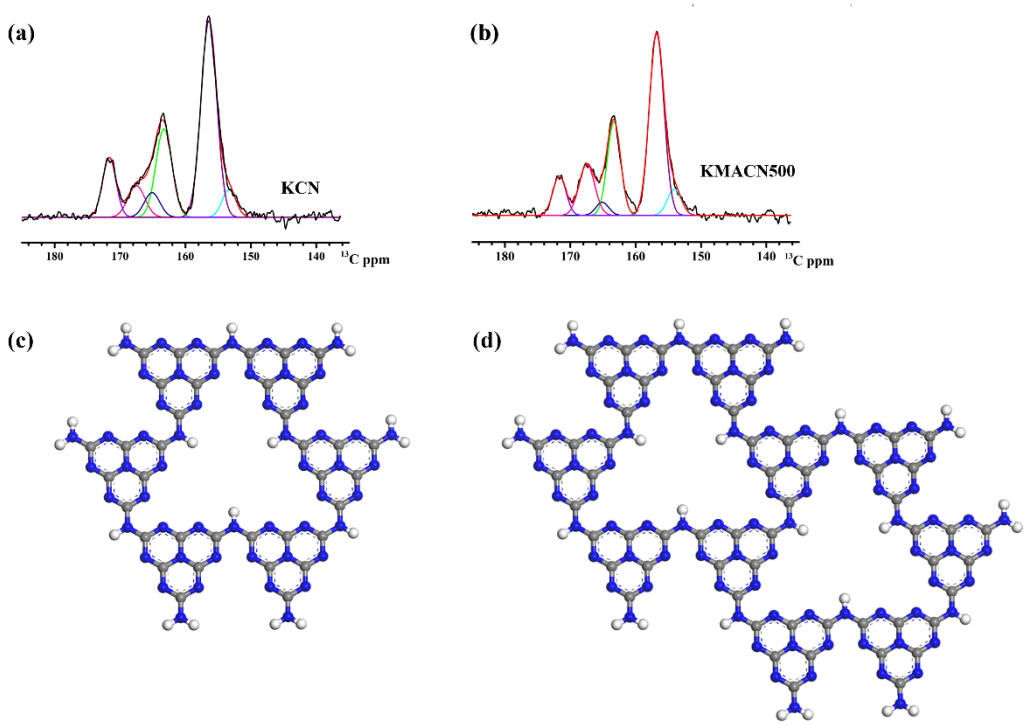

Fig. S7. Deconvolutions of ^{13}C direct excitation spectra of (a) KCN and (b) KMACN500. (c) and (d) molecular structures of HPHIs with different sizes. Hydrogen, carbon, and nitrogen are represented by white, grey, and blue colors.

Table S2. Numbers of C1-C5 in KCN and KMACN500 estimated by area ratios of deconvoluted peaks to C1 (C-N_c) in Fig. S6a and b based on the carbon atom numbers in HPHIs with different sizes.

	C-N_c (C1)	**C-NH (C2)**	**C-NH_2 (C3)**	**C-N^- (C4)**	**C-N-C≡N (C5)**	$\sum_{i=2}^{5} Ci$
KCN	18	8	2	4	4	18
PHI (Fig. S6c)	18	12	6	0	0	18
KMACN500	30	14	2	8	6	30
PHI (Fig. S6d)	30	22	8	0	0	30

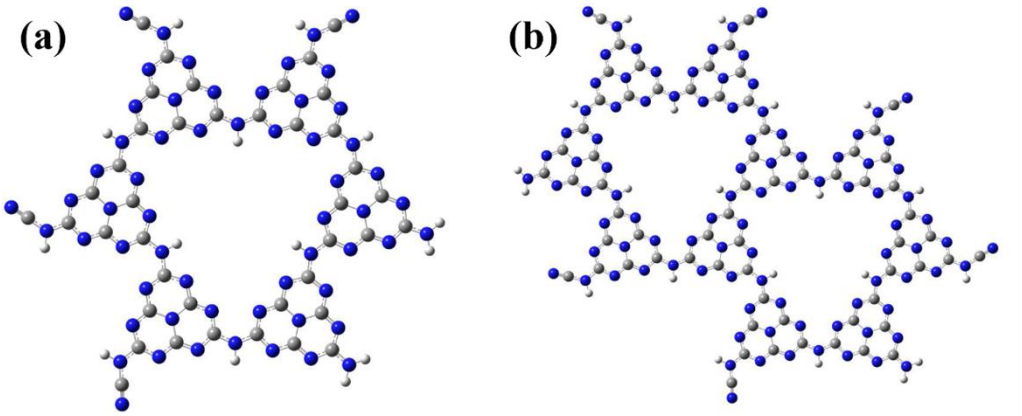

Fig. S8. Optimized structures of cyanamide-functionalized HPHIs corresponding to (a) KCN and (b) KMACN500. Hydrogen, carbon, and nitrogen atoms are represented by white, grey, and blue colors.

Table S3. HOMO energy, LUMO energy and HOMO-LUMO Gap for the optimized molecular models for KCN and KMACN500 shown in Figures 8 and 9.

Optimized Structure	HOMO energy (eV)	LUMO energy (eV)	HOMO-LUMO Gap (eV)
KCN			
KCN_A	-6.38	-3.30	3.08
KCN_B	-6.15	-3.74	2.41
KCN_C	-5.62	-4.09	1.53
KMACN500			
KMACN500_A	-6.39	-3.45	2.94
KMACN500_B	-6.00	-3.56	2.44
KMACN500_C	-5.84	-3.94	1.90
KMACN500_D	-5.23	-4.50	0.73

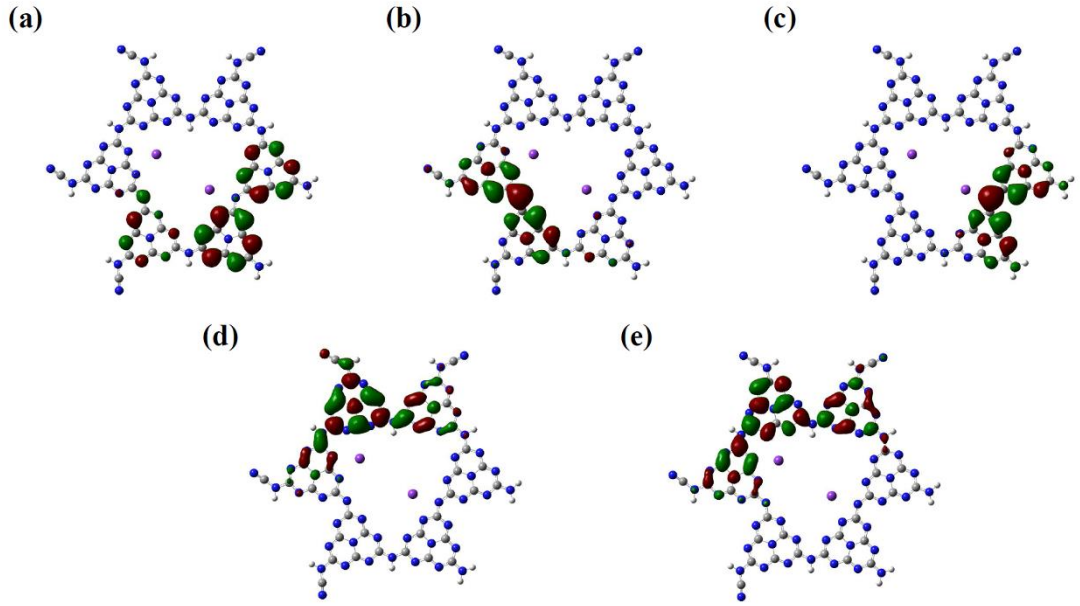

Fig. S9. Frontier molecular orbitals (a) HOMO-2, (b) HOMO-1, (c) HOMO, (d) LUMO, and (e) LUMO+1 for optimized KCN_B. Hydrogen, carbon, nitrogen, and potassium atoms are represented by white, grey, blue, and purple colors. The isosurface value is 0.02 a.u.

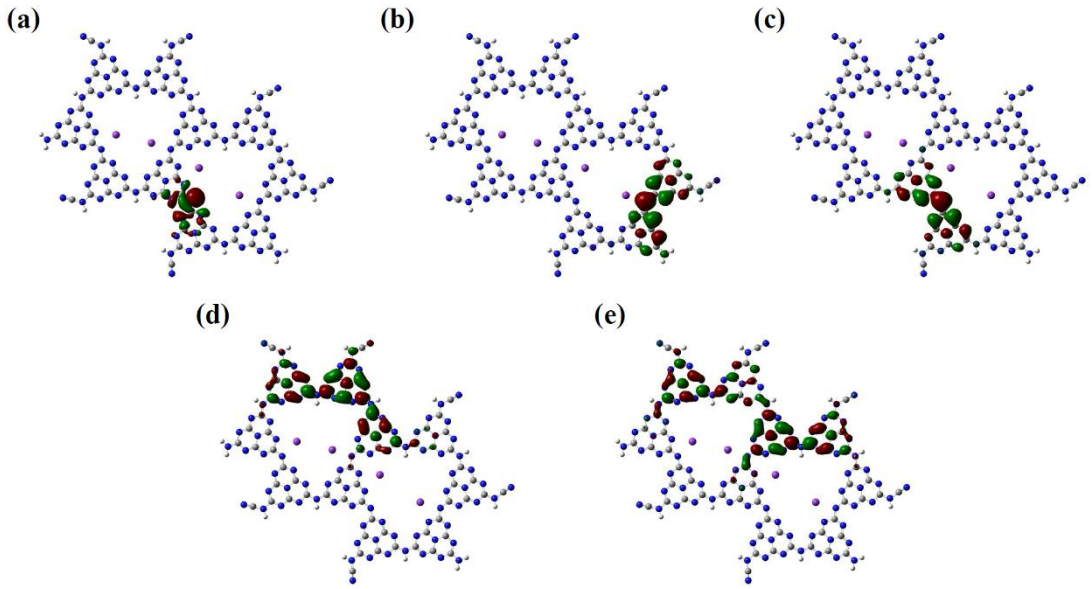

Fig. S10. Frontier molecular orbitals (a) HOMO-2, (b) HOMO-1, (c) HOMO, (d) LUMO, and (e) LUMO+1 for optimized KMACN500_B. Hydrogen, carbon, nitrogen, and potassium atoms are represented by white, grey, blue, and purple colors. he isosurface value is 0.02 a.u.

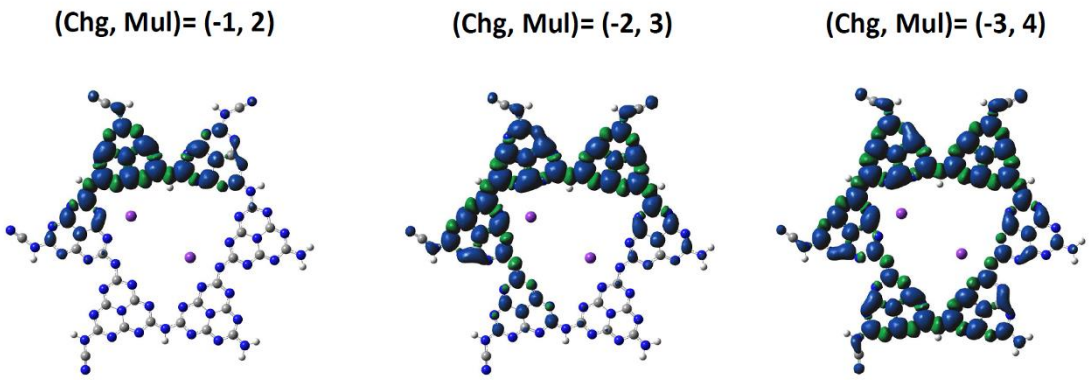

Fig. S11. Spin density distribution for KCN_B at vertical multi-anion states with storage of 1-3 electrons. The isosurface value is 0.0004 a.u.

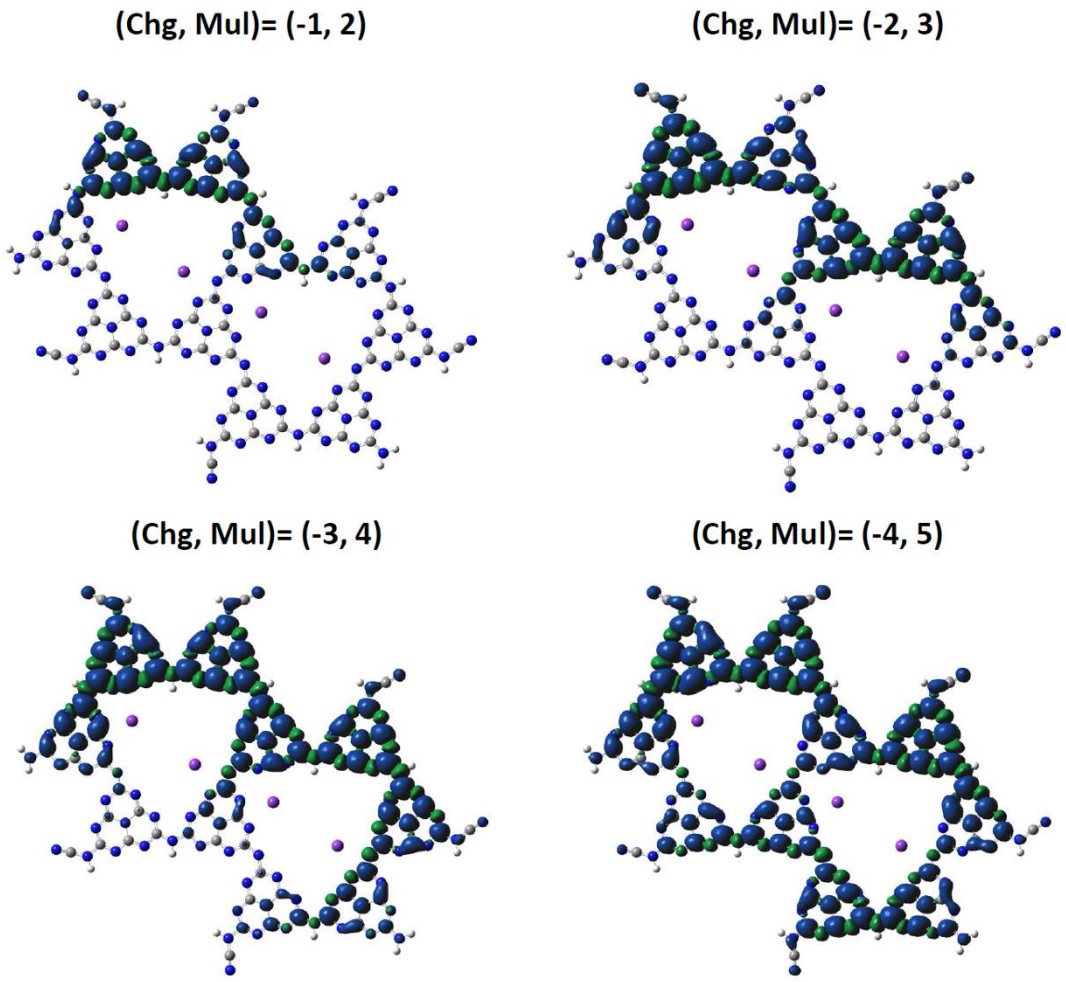

Fig. S12. Spin density distribution for KMACN500_C at vertical multi-anion states with storage of 1-4 electrons. The isosurface value is 0.0004 a.u.