Electronic Supporting Information

Ultrafast Anisotropic Exciton Dynamics in a Water-Soluble Ionic Carbon Nitride Photocatalyst

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Experimental details

K,Na-PHI sample preparation. Aqueous water-soluble carbon nitride simples (2 g/L) are prepared as reported and diluted to the demand concentrations.[1] Its oxygen-free solutions were obtained by freeze-pump-thaw method and kept in an airtight cuvette for the spectroscopic investigation.

Steady-state UV/Vis absorption spectroscopy. The steady-state absorption spectra were measured in 1 cm quartz cuvettes using a Jasco V780 UV/Vis/NIR spectrophotometer.

Time-resolved transient absorption spectroscopy (Tr-TA). A custom-built setup was employed to acquire fs-TA data. The setup is described in detail elsewhere.[2] The pump pulses around 330 nm wavelength generated by a TOPAS amplifier have been used from the fundamental laser with a pulse duration of approximately 100 fs. The repetition rate of the pump pules has been reduced to 0.5 kHz by a mechanical chopper. A white-light supercontinuum probe pulse at 1 kHz repetition rate was generated by focusing a minor part of the output of the Ti:Sapphire amplifier on a rotating CaF_2 plate to probe the absorbance of the sample between 400 to 780 nm. The probe beam was delayed in time with regard to the pump beam by passing through an optical delay line. The polarization is adjusted to the magic angle by a Berek compensator and a polarizer for magic angle TA measurement. While for TA anisotropy TAA test, a single-color probe was generated via a non-collinear optical-parametric amplifier (TOPASwhite, LightConversion Ltd.) and split into two sets after a beam splitter. After setting their polarization parallel and perpendicular to the pump polarization, one portion of each polarized probe beam was sent to a reference photodiode while the other one was allowed to pass through the sample before being recorded by photodiodes purchased from Pascher Instruments AB. From the parallel ($\Delta A_{||}$) and perpendicular ($\Delta A_{\perp}$) transient absorption signals, we can construct the isotropic signal: $\Delta Abs(\lambda,\tau) = \frac{1}{3}(\Delta A_{\parallel}(\lambda,\tau) + 2\Delta A_{\perp}(\lambda,\tau))$ where λ is the probe wavelength and τ is the pump–probe delay time. In addition, the anisotropic signal $r(\lambda,\tau)$ can also be obtained from $r(\lambda,\tau) = \frac{\Delta A_{\parallel}(\lambda,\tau) - \Delta A_{\perp}(\lambda,\tau)}{\Delta A_{\parallel}(\lambda,\tau) + 2\Delta A_{\perp}(\lambda,\tau)}$ and due to the rather poorly compressed UV pulses used at this stage of the experiment, we would mainly focus on the TAA decay kinetics on a ps timescale and longer.

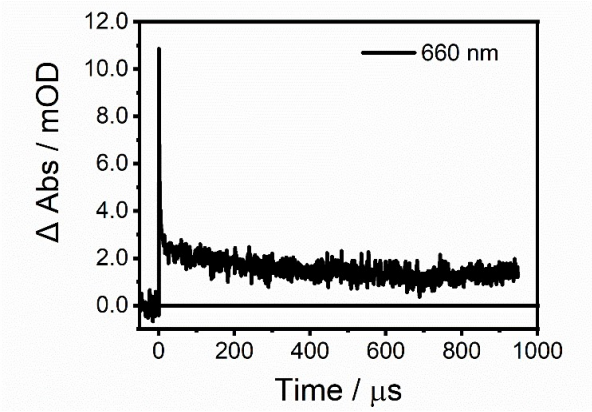

Figure S1. nanosecond-TA decay of aqueous K,Na-PHI probed at 660 nm in the absence of oxygen under 355 nm excitation.

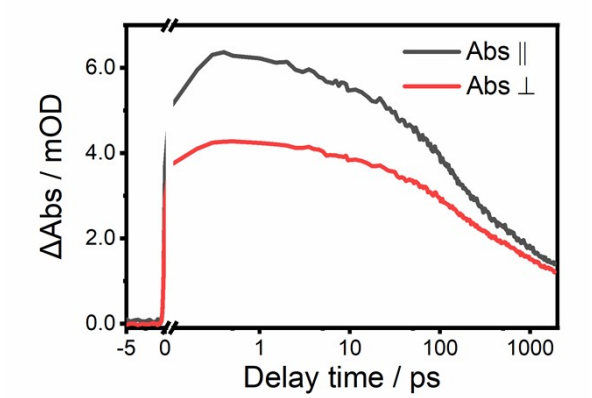

Figure S2. The fs-TA kinetic traces of $\Delta A_{||}$ and ΔA probed at 600 nm in aqueous K,Na-PHI under oxygen-free environment.

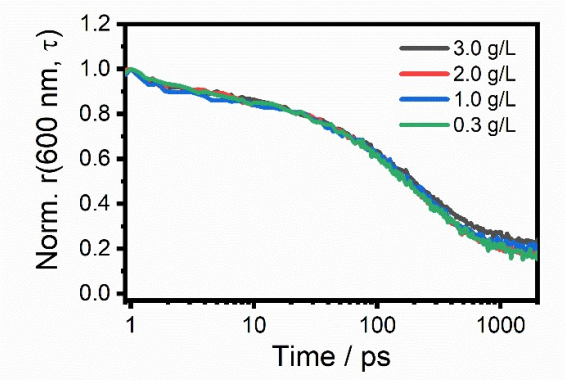

Figure S3. Normalized transient absorption anisotropy TAA traces of aqueous K,Na-PHI in the absence of O_2 probed at 600 nm with various concentrations.

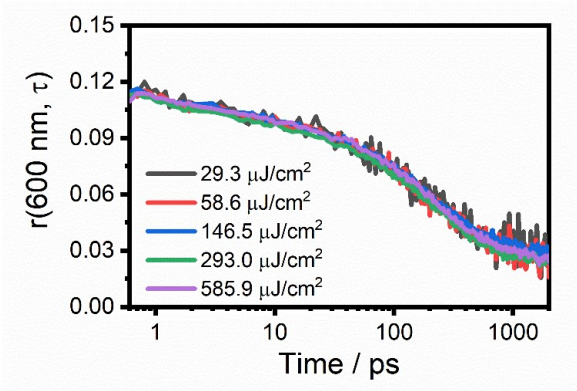

Figure S4. Transient absorption anisotropy TAA traces of aqueous K,Na-PHI (2 g/L) in the absence of O_2 probed at 600 nm with variation of pump fluence.

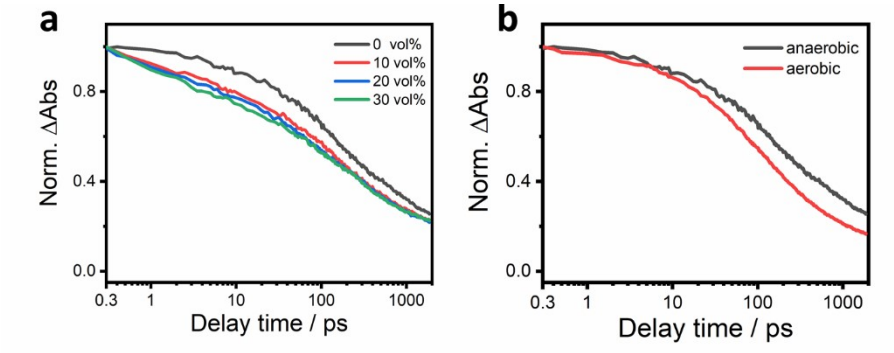

Figure. S5 Transient absorption TAS kinetics of K,Na-PHI dispersed in (a) water-methanol mixtures at various volume ratios in the absence of O_2 and (b) aqueous K,Na-PHI under anaerobic and aerobic conditions upon excitation at 330 nm.

Reference

1. I. Krivtsov, D. Mitoraj, C. Adler, M. Ilkaeva, M. Sardo, L. Mafra, C. Neumann, A. Turchanin, C. Li, B. Dietzek, R. Leiter, J. Biskupek, U. Kaiser, C. Im, B. Kirchhoff, T. Jacob and R. Beranek, *Angew Chem Int Ed Engl*, 2020, **59**, 487-495.
2. R. Siebert, D. Akimov, M. Schmitt, A. Winter, U. S. Schubert, B. Dietzek and J. Popp, *Chemphyschem*, 2009, **10**, 910-919.

