Supplementary information for

Light Harvesting and Energy Transfer in a Porphyrin-based Metal Organic Framework

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1. Thermogravimetric analysis

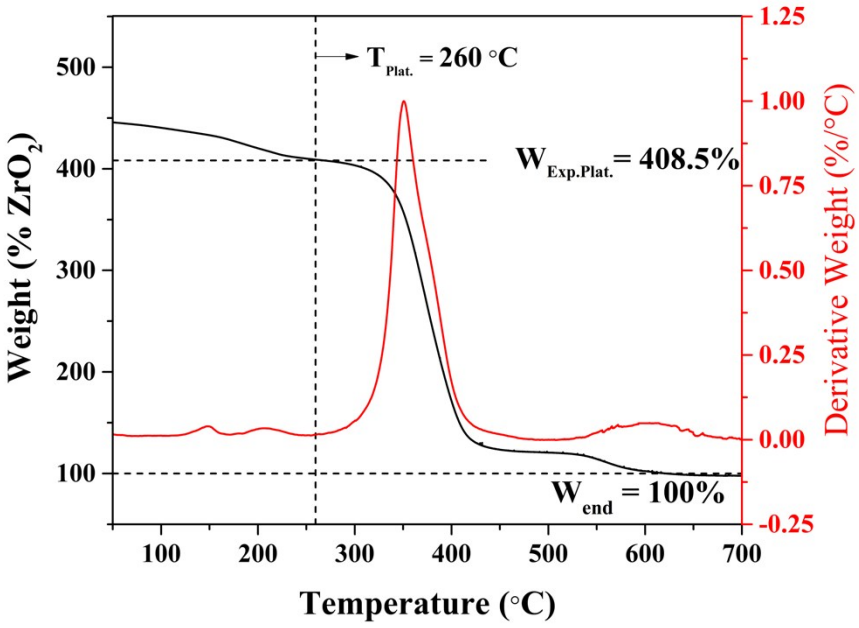


Figure S1. TGA plot of PCN-223(fb)

The reaction for the complete combustion of ideal (defect-free), hydroxylated PCN-223 MOF is-

$$Zr_6O_4(OH)_4(TCPP)_3\ (s) + 154.5\ O_2\ (g) \rightarrow 6\ ZrO_2\ (s) + 144\ CO_2\ (g) + 41\ H_2O\ (g)$$

$$\frac{moles\ of\ Zr_6O_4(OH)_4(TCPP)_3}{moles\ of\ ZrO_2} = \frac{1}{6}$$

$$\text{moles of } Zr_6O_4(OH)_4(TCPP)_3 = \frac{moles\ of\ ZrO_2}{6}$$

$$\left(\frac{W_{TGA\ plateau}}{W_{end}}\right)_{theoretical} = \frac{MW_{Zr_6O_4(OH)_4(TCPP)_3}}{6 \times MW_{ZrO_2}}$$

$$\left(\frac{W_{TGA\ plateau}}{W_{end}}\right)_{theoretical} = \frac{3039.57}{6 \times 123.22}$$

$$\left(\frac{W_{TGA\ plateau}}{W_{end}}\right)_{theoretical} = 4.11$$

If the end weight of the TGA run is normalized to 100%, then for hydroxylated, defect-free, solvent-free PCN-223 material, the experimental TGA plateau should be found at 411% on the TGA curve. By using the experimental $\left(\frac{W_{TGA\ plateau}}{W_{end}}\right)$ ratio, the effective molecular weight of a MOF can be calculated,

$$MW_{effective} = \left(\frac{W_{TGA\ plateau}}{W_{end}}\right)_{experimental} \times 6 \times MW_{ZrO_2}$$

For PCN-223, $\left(\frac{W_{TGA\ plateau}}{W_{end}}\right)_{experimental} = \mathbf{4.085}$

$$MW_{effective} = 4.085 \times 6 \times 123.2 = 3019.6$$

The general molecular formula for a hydroxylated PCN-223 MOF in which modulator loss has not occurred is $Zr_6O_4(OH)_4(TCPP)_x(Mod)_{([Mod]/[Ligand])x}$. The value of x in this formula can be determined by,

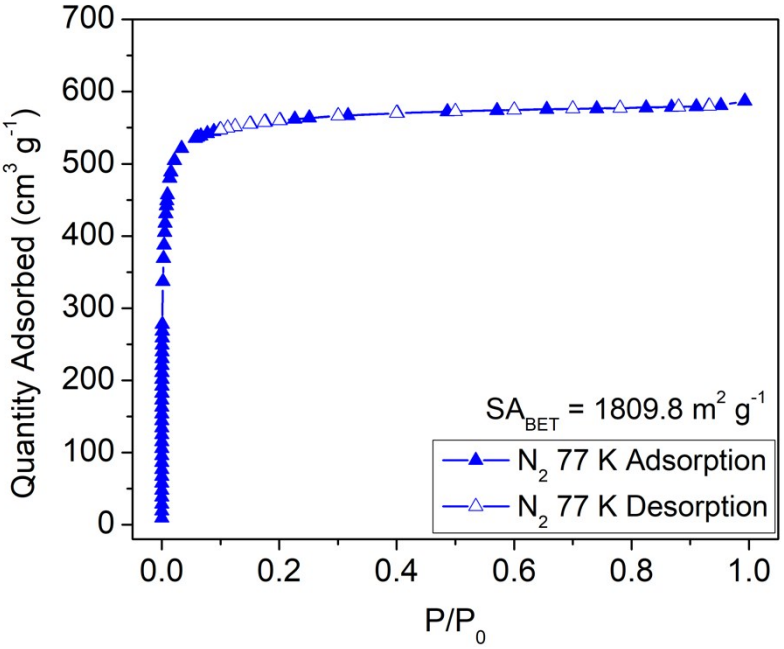
$$x = \frac{MW_{effective} - 547.2 - 64 - 68}{786.79 + MW_{Modulator} \times ([Mod]/[Ligand])}$$

The modulator to ligand molar ratio in the framework ([Mod]/[Ligand]) for PCN-223 was found to be is 1.48 (from ^{1}H NMR analysis).

$$x = \frac{3019.6 - 547.2 - 64 - 68}{786.79 + (74.08 \times 1.48)} = \mathbf{2.61}$$

The resulting molecular formula of the MOF is $\mathbf{Zr_6O_4(OH)_4(TCPP)_{2.61}(Mod)_{3.84}}$

Propionic acid (PA) is the modulator used in the synthesis. Therefore, the molecular formula of MOF is $\mathbf{Zr_6O_4(OH)_4(TCPP)_{2.61}(PA)_{3.84}}$



2. Nitrogen gas adsorption isotherm

Figure S2. N_2 gas adsorption isotherm of PCN-223(fb)

The BET surface area of the MOF was found to be 1809.8 m^2 g^{-1}.

3. Acid-base titration curves of TCPP and PCN-223(fb)

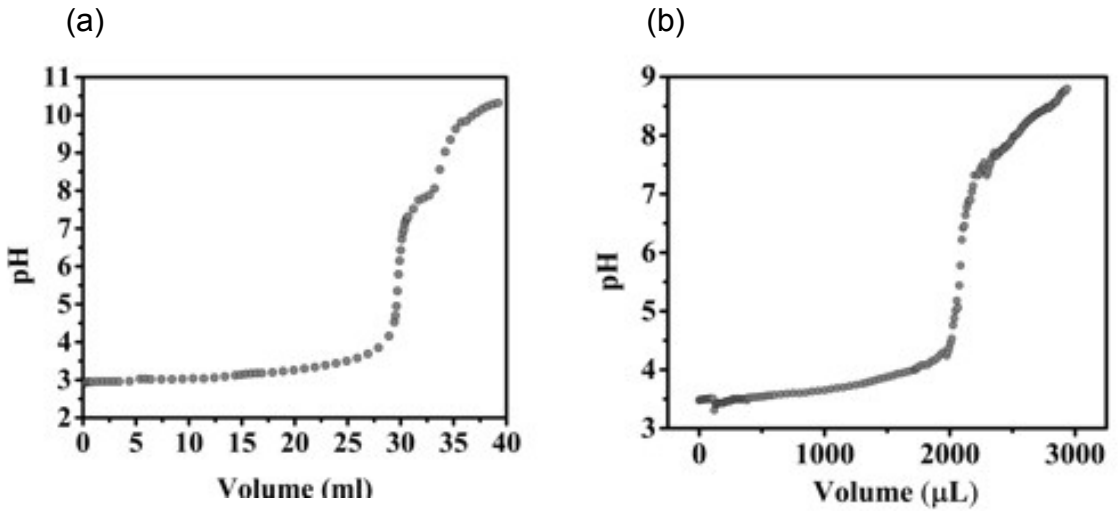


Figure S3. (a) Titration curve of TCPP in water (10^{-6}M) against 0.01 M NaOH solution. The first and second equivalence points of titration are around pH 5.54 and 7.5 respectively (b) Titration curve of PCN-223(fb) in water against 0.01 M NaOH solution. The equivalence point of titration is around pH 5.70.

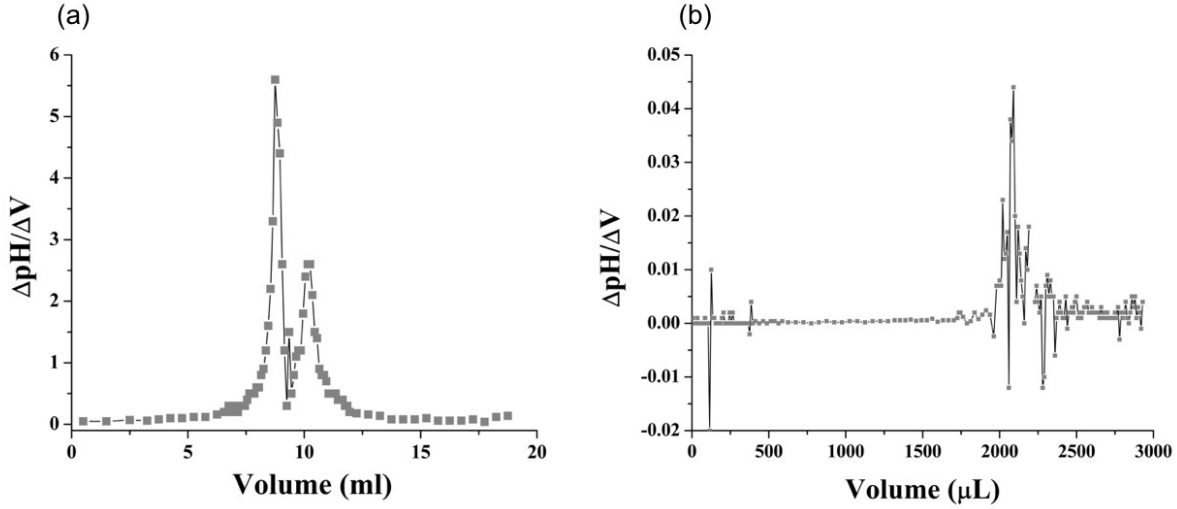


Figure S4. (a) First derivative of the titration curve for TCPP as a function of volume of titrant (b) First derivative of the titration curve for PCN-223(fb) as a function of volume of titrant.

4. Absorption data for TCPP and PCN-223(fb)

Table 1. Positions of Soret (B) band and Q bands in the diffused absorption spectra of TCPP and PCN-223(fb)

	B(Soret)	$Q_y(1,0)$	$Q_y(0,0)$	$Q_x(1,0)$	$Q_x(0,0)$

TCPP	425nm	525nm	561nm	597nm	652nm
PCN-223(fb)	412nm	524nm	561nm	595nm	652nm

5. Determination of $[HP^{2+}]/[P]$ in TCPP solutions and MOF suspensions

The ratio of the concentration of protonated porphyrins to that of neutral porphyrins in TCPP solutions and MOF suspensions was determined using Henderson-Hasselbalch equation.

$$pH = pK_a + \log_{10}([P]/[HP^{2+}])$$

$$[P]/[HP^{2+}] = 10^{pH - pK_a}$$

$$[HP^{2+}]/[P] = \frac{1}{10^{(pH - pK_a)}}$$

6. Emission spectra of TCPP and PCN-223 as a function of temperature

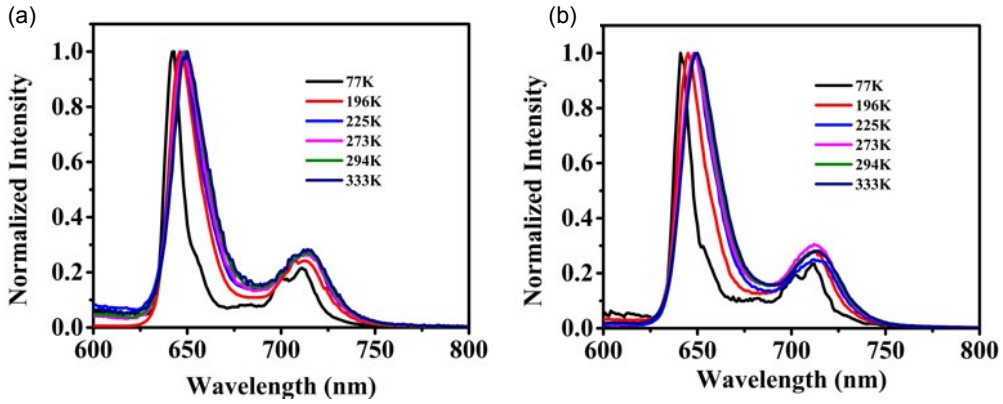
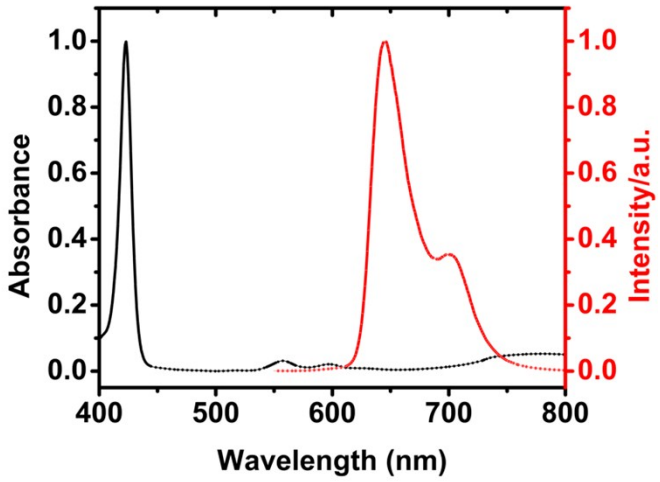


Figure S5. (a) Steady-state emission spectra of TCPP as a function of temperature (b) Steady-state emission spectra of PCN-223(fb) as a function of temperature.

7. Spectral overlap integral calculation

$$J(\lambda) = \int_0^{\infty} \varepsilon_A(\lambda)\, \lambda^4\, F_D(\lambda)\, d\lambda$$

where ε_A is the extinction coefficient spectrum of the acceptor in units of $M^{-1}cm^{-1}$, λ is the wavelength in nm and F_D is the wavelength dependent donor emission spectrum normalized to



an area of 1.

Figure S6. Spectral overlap between the absorption spectrum of protonated TCPP (acceptor) and emission spectrum of neutral TCPP (donor)

The spectral overlap integral was estimated to be $5.344 \times 10^{-14}\ M^{-1}cm^3$.

8. Quantum yield calculation

The relative quantum yield of donor (neutral TCPP) in the absence of acceptor (protonated TCPP) was calculated using,

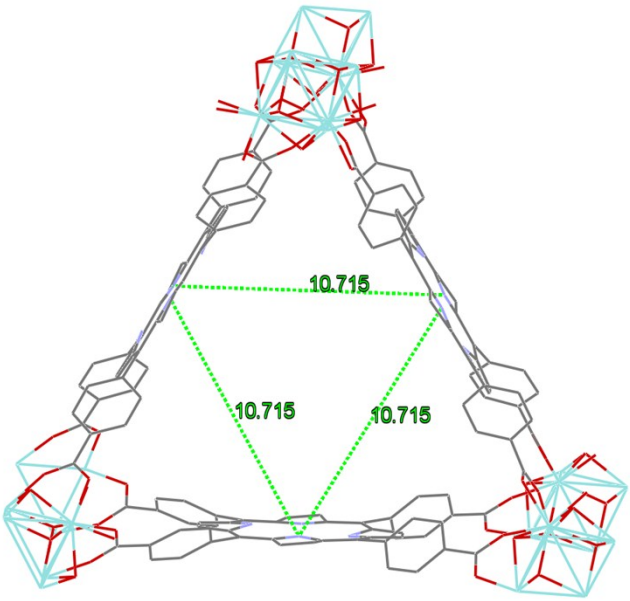
$$\frac{Q}{Q_R} = \frac{I}{I_R} \times \frac{OD_R}{OD} \times \frac{\eta^2}{\eta_R^2}$$

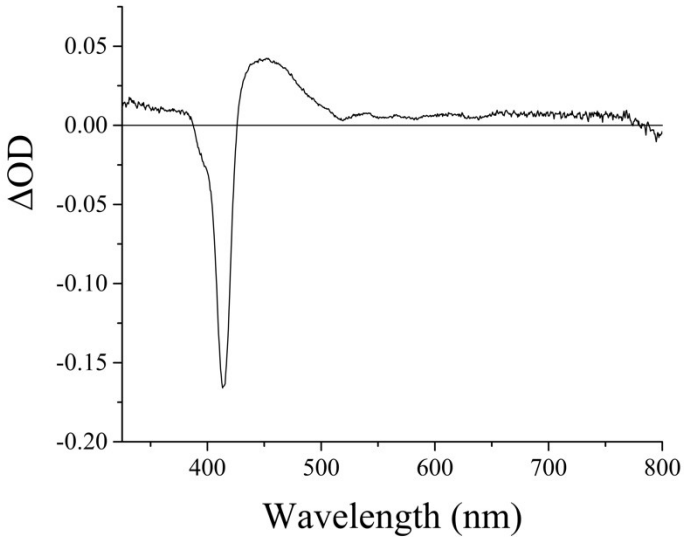
where Q is the quantum yield, I is the integrated intensity, η is the refractive index, and OD is the optical density. The subscript R refers to the reference fluorophore of known quantum yield.

Quantum yield of neutral TCPP in methanol (reference) = 0.09.

Quantum yield of neutral TCPP (in water) was estimated to be 0.27 ± 0.035.

9. Center-to-Center donor-acceptor distance in PCN-223 framework (10.715 Å)





10. (a)Transient absorption difference spectra of TCPP

(b) Transient absorption difference spectra of PCN-223

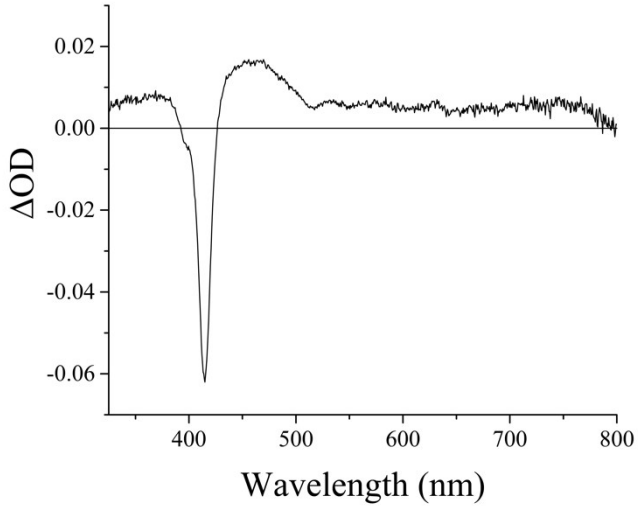


Figure S8. Transient absorption difference spectra of (a) TCPP and (b) PCN-223(fb) measured in degassed water at room temperature following 532 nm pulsed laser excitation (4-5 mJ/pulse, 5−7 ns fwhm). Both difference spectra represent an average of 30 transients.

11. Comparison between nanosecond TA and femtosecond TA difference spectra

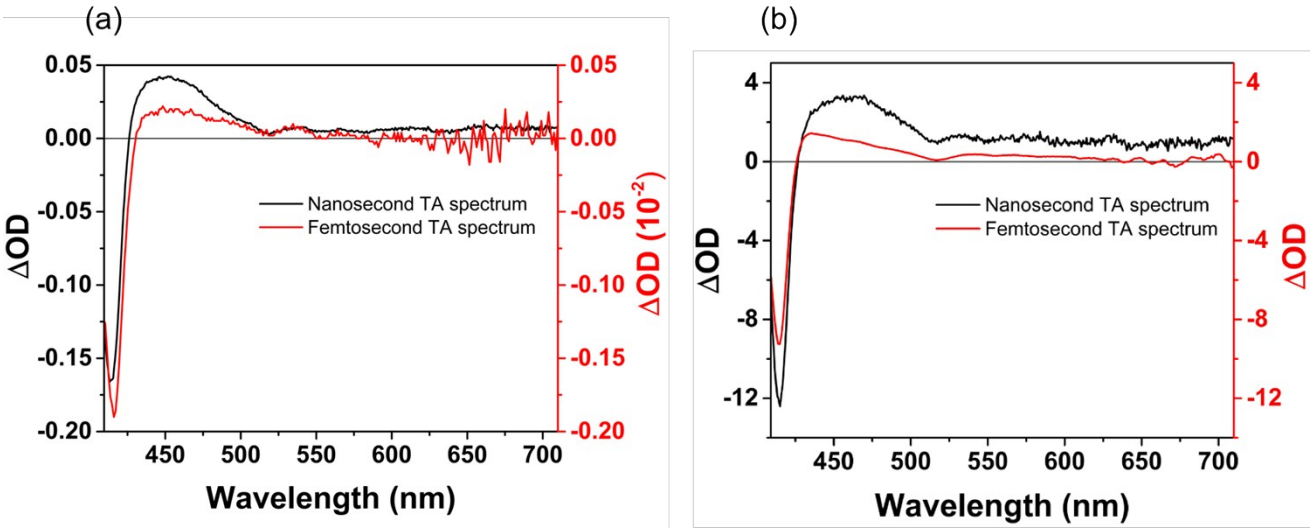


Figure S9. Comparison between the femtosecond TA (at a time delay of 5.5 ns) and nanosecond TA difference spectra (collected promptly after laser excitation) of (a) TCPP and (b) PCN-223(fb).

12. Kinetic analysis of the ultrafast data

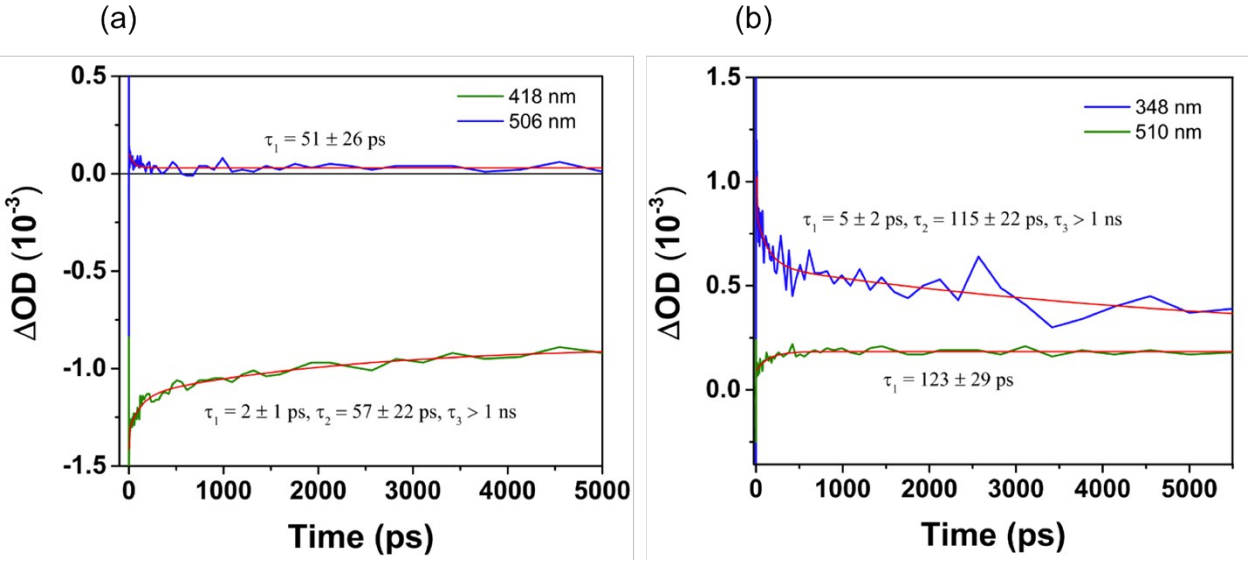


Figure S10. Transient absorption kinetic traces of (a) TCPP in 1:1 water-ethanol (v/v) mixture (pH-8) and (b) PCN-223(fb) in water (pH-8) following 400 nm pulsed laser excitation (140 fs fwhm) at probe wavelengths indicated in the legend. Time components of the kinetic traces obtained from fitting are shown in the figure.