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Electronic Supplementary Information for

Electronic relaxation dynamics of PCDA-PDA studied by transient absorption spectroscopy

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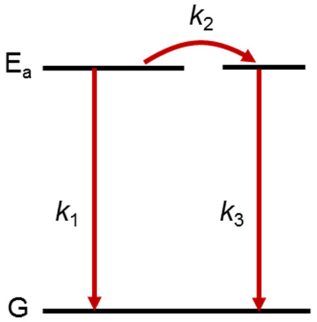
Contents

1. Rate equations and analytical solutions for kinetic models

For each kinetic model in Figure 4, coupled differential equations are written and analytically solved to obtain the time-dependent populations of the electronic states involved in the population relaxation of the excited PCDA-PDA.

1-a. KM-1



The coupled differential equations for KM-1 are given by

$$\frac{d[\mathrm{E_a}]}{dt} = -(k_1 + k_2)[\mathrm{E_a}]$$

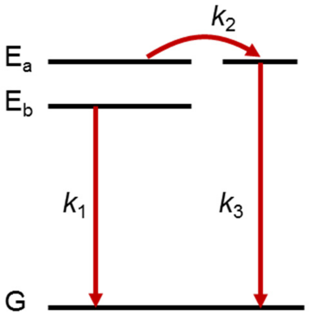
$$\frac{d[\mathrm{I}]}{dt} = k_2[\mathrm{E_a}] - k_3[\mathrm{I}]$$

The analytical solutions are obtained by using $[\mathrm{E_a}]_0=1$,

$$[\mathrm{E_a}] = e^{-(k_1+k_2)t}$$

$$[\mathrm{I}] = \frac{k_2 e^{-(k_1+k_2+k_3)t}(e^{(k_1+k_2)t} - e^{k_3 t})}{k_1 + k_2 - k_3}$$

1-b. KM-2



The coupled differential equations for KM-2 are given by

$$\frac{d[\mathrm{E_a}]}{dt} = -k_2[\mathrm{E_a}]$$

$$\frac{d[\mathrm{E_b}]}{dt} = -k_1[\mathrm{E_b}]$$

$$\frac{d[\mathrm{I}]}{dt} = k_2[\mathrm{E_a}] - k_3[\mathrm{I}]$$

The analytical solutions are obtained by using the boundary condition, $[\mathrm{E_a}]_0=[\mathrm{E_b}]_0=1/2$,

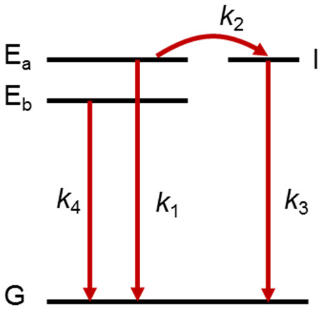
$$[\mathrm{E_a}] = \frac{1}{2}e^{-k_2 t}$$

$$[\mathrm{E_b}] = \frac{1}{2}e^{-k_1 t}$$

$$[\mathrm{I}]=\frac{k_1\left(e^{-k_3 t}-e^{-k_2 t}\right)}{2(k_2-k_3)}$$

1-c. KM-3

The coupled differential equations for KM-3 are given by



$$\frac{d[\mathrm{E_a}]}{dt}=-(k_1+k_2)[\mathrm{E_a}]$$

$$\frac{d[\mathrm{E_b}]}{dt}=-k_4[\mathrm{E_b}]$$

$$\frac{d[\mathrm{I}]}{dt}=k_2[\mathrm{E_a}]-k_3[\mathrm{I}]$$

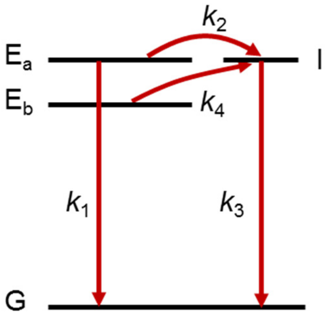
The analytical solutions are obtained by using the boundary condition, $[\mathrm{E_a}]_0=[\mathrm{E_b}]_0=1/2$,

$$[\mathrm{E_a}]=\frac{1}{2}e^{-(k_1+k_2)t}$$

$$[\mathrm{E_b}]=\frac{1}{2}e^{-k_4 t}$$

$$[\mathrm{I}]=\frac{k_2 e^{-(k_1+k_2+k_3)t}\left[e^{(k_1+k_2)t}-e^{k_3 t}\right]}{2(k_1+k_2-k_3)}$$

1-d. KM-4



The coupled differential equations for KM-4 are given by

$$\frac{d[\mathrm{E_a}]}{dt}=-(k_1+k_2)[\mathrm{E_a}]$$

$$\frac{d[\mathrm{E_b}]}{dt}=-k_4[\mathrm{E_b}]$$

$$\frac{d[\mathrm{I}]}{dt}=k_2[\mathrm{E_a}]+k_4[\mathrm{E_b}]-k_3[\mathrm{I}]$$

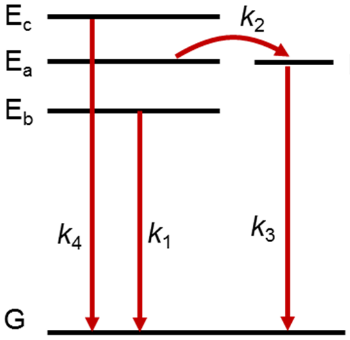
The analytical solutions are obtained by using the boundary condition, $[\mathrm{E_a}]_0=[\mathrm{E_b}]_0=1/2$,

$$[\mathrm{E_a}]=\frac{1}{2}e^{-(k_1+k_2)t}$$

$$[\mathrm{E_b}]=\frac{1}{2}e^{-k_4 t}$$

$$[\mathrm{I}] = e^{-(k_1+k_2+k_3+k_4)t}\left[\frac{k_4 e^{(k_3+k_4)t}}{2(k_1+k_2-k_3)} + \frac{k_2 e^{(k_1+k_2+k_3)t}}{2(k_4-k_3)} + \frac{(k_1k_4 - k_3k_4 + 2k_2k_4 - k_2k_3)e^{(k_1+k_2+k_4)t}}{2(k_3-k_4)(k_1+k_2-k_3)}\right]$$

1-e. KM-5



The coupled differential equations for KM-5 are given by

$$\frac{d[\mathrm{E_a}]}{dt} = -k_2[\mathrm{E_a}]$$

$$\frac{d[\mathrm{E_b}]}{dt} = -k_1[\mathrm{E_b}]$$

$$\frac{d[\mathrm{E_c}]}{dt} = -k_4[\mathrm{E_c}]$$

$$\frac{d[\mathrm{I}]}{dt} = k_2[\mathrm{E_a}] - k_3[\mathrm{I}]$$

The analytical solutions are obtained by using the boundary condition, $[\mathrm{E_a}]_0=[\mathrm{E_b}]_0=[\mathrm{E_c}]_0=1/3$,

$$[\mathrm{E_a}] = \frac{1}{3}e^{-k_2 t}$$

$$[\mathrm{E_b}] = \frac{1}{3}e^{-k_1 t}$$

$$[\mathrm{E_c}] = \frac{1}{3}e^{-k_4 t}$$

$$[\mathrm{I}] = \frac{k_2 e^{-(k_2+k_3)t}(e^{k_2 t} - e^{k_3 t})}{3(k_2-k_3)}$$

2. Global fitting analysis of the TA signals

The TA signals in Figure 3 contain all dynamic information on the electronic relaxation of PCDA-PDA. Here, we used the global fitting analysis to extract all dynamical information from the TA signals. In the global fitting analysis, the TA signal (**D**) can be expressed by the product of the time-dependent populations (**C**) and their corresponding spectral components ($\mathbf{S}^{\mathrm{T}}$),

$$\mathbf{D} = \mathbf{C} \cdot \mathbf{S}^{\mathrm{T}} \tag{2}$$

where the columns of matrix (**C**, sized $m \times k$) are the time-dependent populations of the k^{th} components at the time delay of m and the rows of matrix ($\mathbf{S}^{\mathrm{T}}$, sized $k \times n$) are the corresponding k^{th} spectra as a function of wavelength n. And m, k, and n represent the time delay, the number of components, and the spectra, respectively. The detailed procedure of the global fitting analysis by using Matlab codes has been reported elsewhere.[1-5] Briefly, the coupled differential equations for the time-dependent populations of individual species are written based on the kinetic models in Figure 4, and the analytical solutions for the time-dependent populations are obtained. The TA signals are written as the sum of the individual components with their spectra and time-dependent populations.

For a given kinetic model, the time-dependent populations (**C**) are calculated with the initial rate constants. The corresponding spectral components ($\mathbf{S}^{\mathrm{T}}$) are obtained by the product of the pseudo-inverse matrix of **C** and **D**,

$$\mathbf{S}^{\mathrm{T}} = \mathbf{C}^{-1} \cdot \mathbf{D} \tag{3}$$

The fitted TA signal ($\mathbf{D}^{\text{fitted}}$) is constructed by the product of **C** and $\mathbf{S}^{\mathrm{T}}$,

$$\mathbf{D}^{\text{fitted}} = \mathbf{C} \cdot \mathbf{S}^{\mathrm{T}} \tag{4}$$

The best fitted data were obtained by iteratively varying the rate constants until the difference between the experimental data ($\mathbf{D}^{\mathrm{exp}}$) and the fitted data ($\mathbf{D}^{\mathrm{fitted}}$) was minimized. [1-3]

As schematically illustrated in Figure S1, the TA signal (**D**) is decomposed into the individual components by the global fitting analysis. The TA signals of PCDA-PDA at 20 and 80 °C are decomposed into three components (E_a, E_b, and I) based on KM-3 and two components (E_a and E_b) based on KM-6, respectively. The spectra and time-dependent populations of individual components are presented in the top and left panels, respectively. The individual components are well distinct in terms of their spectra and time-dependent populations.

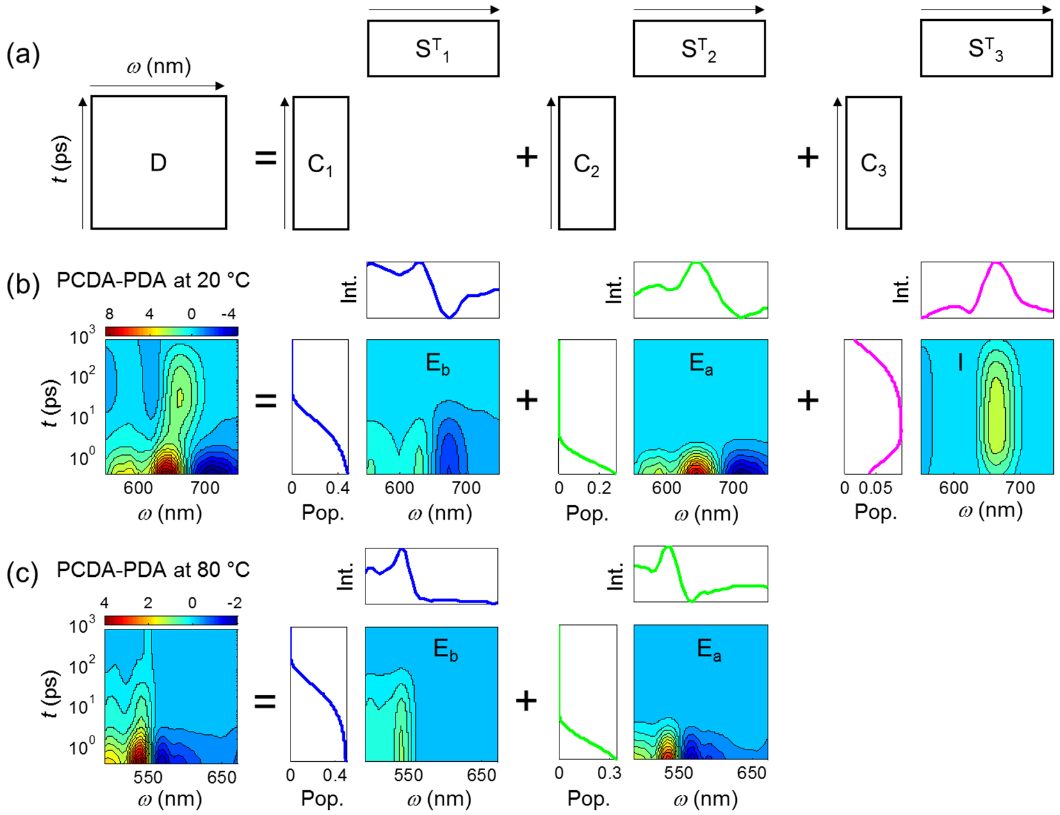


Figure S1. (a) Illustration of the global fitting analysis of the TA signal. The TA signal ($\mathbf{D} = \mathbf{C} \cdot \mathbf{S}^{\mathrm{T}}$) is decomposed into their individual components with the corresponding time-dependent population ($\mathbf{C}_{\mathrm{J}}$) and spectrum ($\mathbf{S}_{\mathrm{J}}^{\mathrm{T}}$) by the global fitting analysis using the kinetic models. (b) PCDA-PDA at 20 °C by using KM-3. (c) PCDA-PDA at 80 °C by using KM-6.

3. Transient absorption (TA) experimental setup

In transient absorption (TA) experiments, the molecule in the sample solution is electronically excited by the visible pump pulse at 530 nm or 630 nm and the subsequent electronic relaxation is probed by the white light probe. A schematic drawing of transient absorption setup is shown below. 800 nm pulse from our femtosecond Ti:Sa oscillator and amplifier system is used to pump the optical parametric amplifier (OPA) which generates the signal and idler in the near IR region. The visible pump pulse is generated by the second harmonic generation of the signal. The white light probe is generated by focusing the 800 nm pulse onto 2 mm thick sapphire disk (c-cut) which covers from 450 nm to 750 nm.

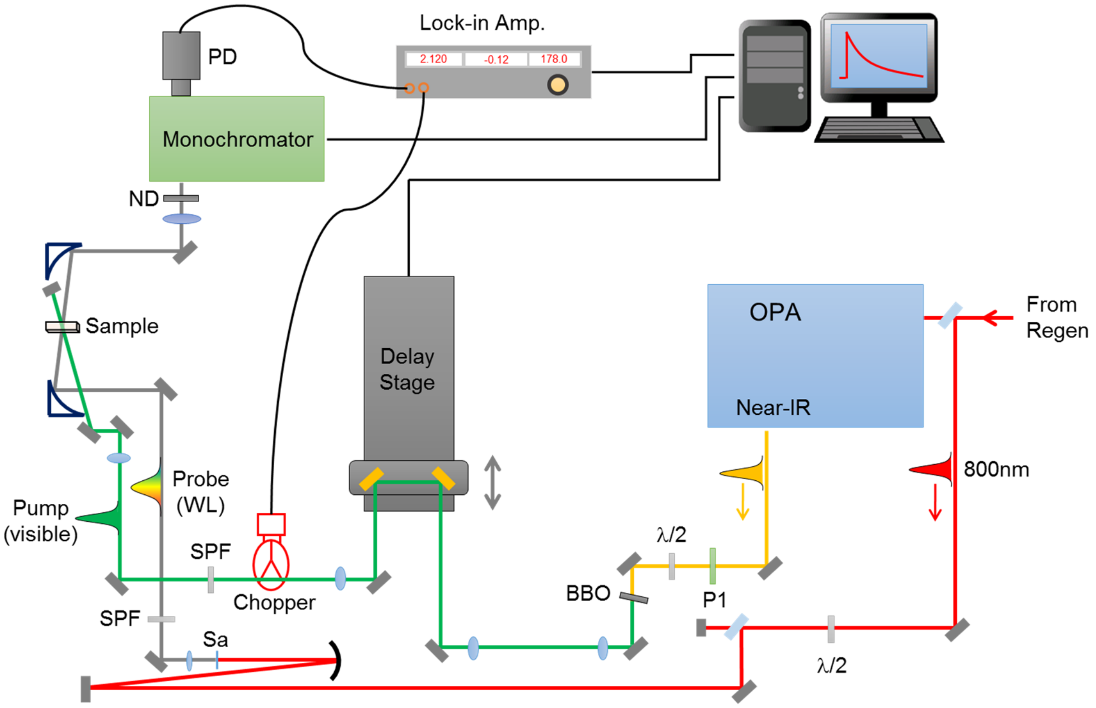


Figure S2. A schematic drawing of our TA experimental setup. ND, neutral density filter; SPF, shortwave-pass filter; Sa, sapphire disk; BBO, *β*-barium borate; P1, polarizer; λ/2, half-wave plate; PD, photodiode; OPA, optical parametric amplifier.

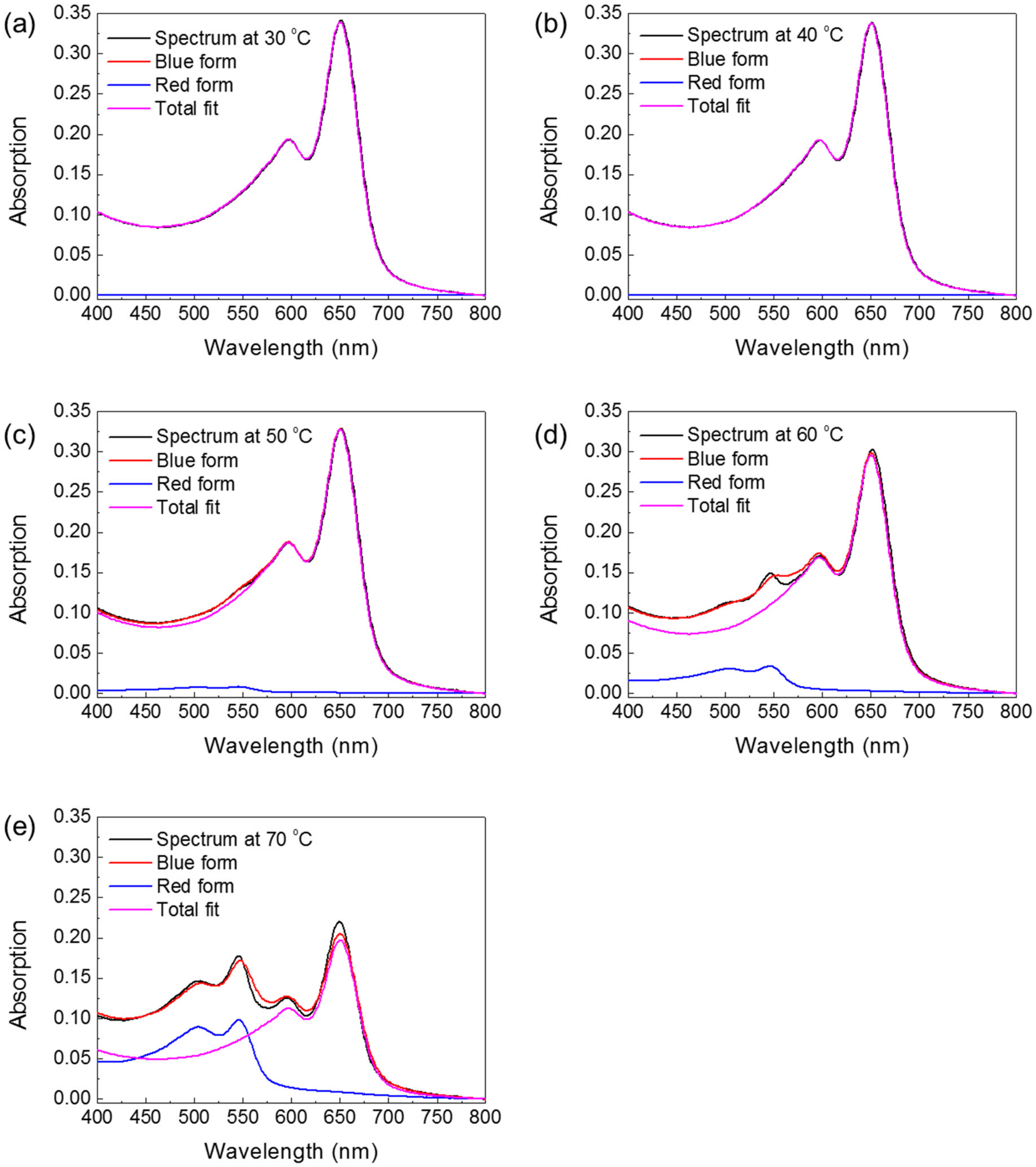


Figure S3. UV-visible spectra of PCDA-PDA measured at 20°C after the temperature cycle are decomposed into the blue and red forms which are approximately identical to the UV-visible spectra of PCDA-PDA at 20 and 80 °C, respectively.

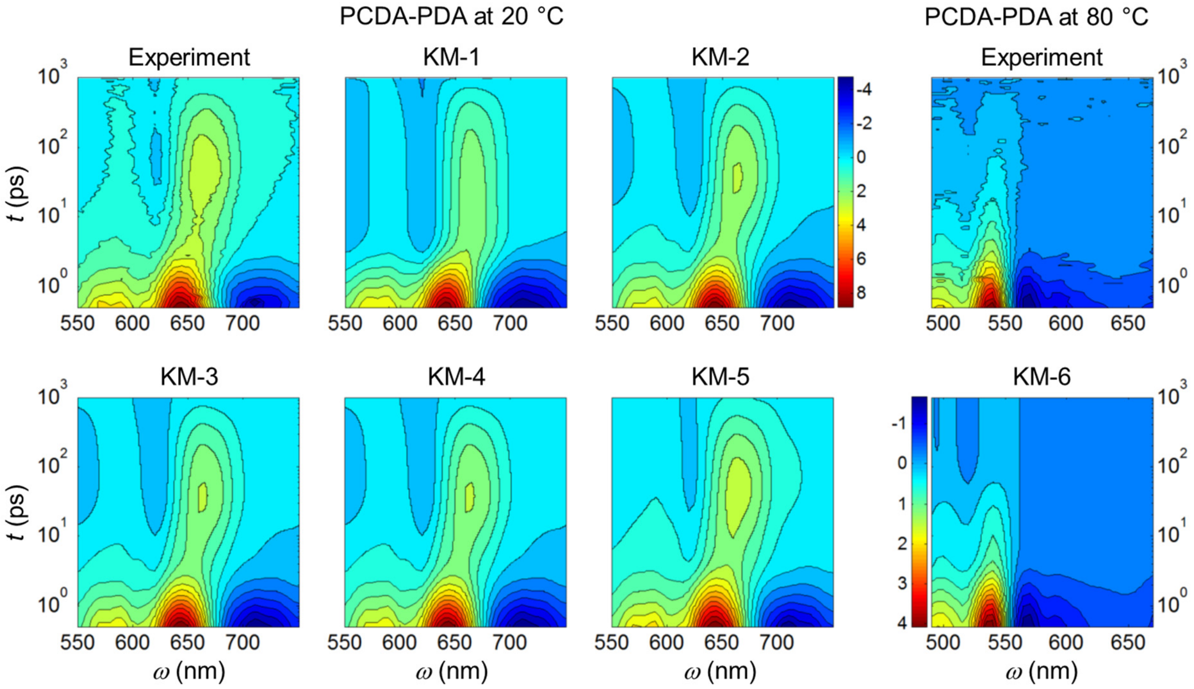


Figure S4. Experimental TA signals and the TA signals fitted by different kinetic models.

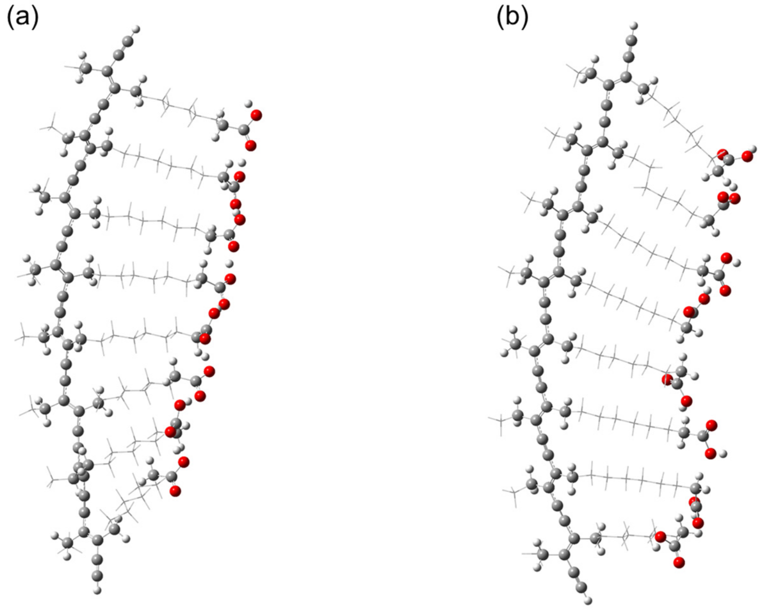


Figure S5. The molecular structure and ONIOM (QM/MM) scheme for model PCDA-PDA (a) with and (b) without H-bonds.

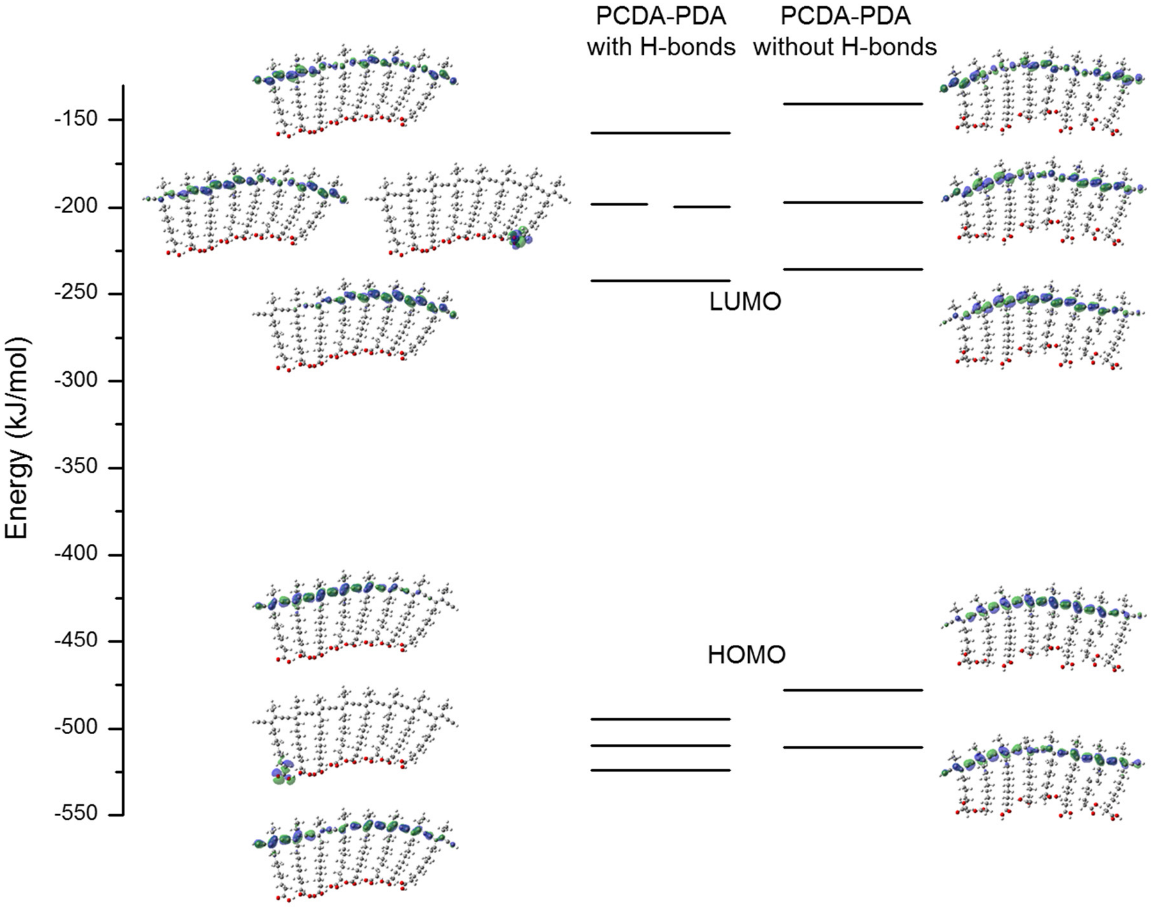


Figure S6. The molecular orbitals (MOs) near the HOMO and LUMO levels of model PCDA-PDA. The quantum chemical calculations were conducted using the density functional theory (DFT) method (b3lyp) and a 3-21g basis set as implemented in the Gaussian 09 package.

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9. References

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