Supporting Information for

Origin of the Reversible Thermochromic Properties of Polydiacetylenes Revealed by Ultrafast Spectroscopy

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1. Transient absorption experimental setup

Our transient absorption (TA) experiments setup is presented in Figure S1. In our TA experimental setup, 800 nm pulse with 0.5 mJ was used to pump the OPA to produce the signal and idler in the range of 1.2 ~ 2.4 nm and the second harmonic of the signal and the fourth harmonic of the idler produce the wavelength in the visible range. The pump beam went through the motorized linear delay stage and its relative time delay with respect to the probe beam was controlled. A small fraction of 800 nm from the regen amplifier was split to generate the white light continuum in a 2 mm thick sapphire disk which used as the probe beam.

Figure S1. Schematic of transient absorption (TA) experimental setup. ND, Neutral density fileter; F, Pass filter; PD, Photodiode; CCD, charge-coupled detector; OPA, optical parametric amplifier; Regen, regenerated amplifier.
2. Kinetic models

To describe the electronic relaxation of excited PDAs, the kinetic model in Figure S2 is used. It is assumed that PDAs are excited to the nearly degenerated electronic states (E\textsubscript{1} and E\textsubscript{2}) by a strong pump pulse. Subsequently, the excited PDAs relax back to the ground state.

![Kinetic models](image)

**Figure S2.** Kinetic models to describe the electronic relaxation of PDAs with (a) reversible and (b) irreversible thermochromic property.

In the kinetic model in Figure S2(a), the time-dependent populations of E\textsubscript{1}, E\textsubscript{2}, and I states can be calculated by the following coupled differential equations,

\[ \frac{d[E_1]}{dt} = -k_1[E_1], \]  
\[ \frac{d[E_2]}{dt} = -k_2[E_2], \]  
\[ \frac{d[I]}{dt} = k_1[E_1] - k_3[I] \]

The analytical solutions of the above differential equations are readily obtained as

\[ [E_1] = [E_1]_0 e^{-k_1t}, \]  
\[ [E_2] = [E_2]_0 e^{-k_2t}, \]  
\[ [I] = \frac{k_1[E_1]_0 [e^{-k_1t} - e^{-k_3t}]}{k_1 - k_3} \]
Here, it is assumed that $[E_1]_0 = [E_2]_0 = 0.5$ and $[I]_0 = 0$ at $t=0$ ps. Eqn (S4)-(S6) represent the time-dependent populations of $E_1$, $E_2$, and $I$ states in the electronic relaxation of PDAs with reversible thermochromic property. The kinetic model in Figure S2(b) can be used to represent the electronic relaxation of PDAs with irreversible thermochromic properties. The time-dependent populations of $E_1$ and $E_2$ states are simply given by Eqn (S1) and (S2) and their analytical solutions in Eqn (S4) and (S5) are used.

3. Global fitting method

Frequency-resolved transient absorption (FRTA) signal includes all the time-dependent spectral components and can be decomposed to the individual components by using the global fitting method. Figure S3 illustrates the decomposition of FRTA signal to the individual components by the global fitting method.

**Figure S3.** Illustration of the decomposition of the FRTA signal ($D = C \cdot S^T$) to three individual components with different time-dependent population ($C_j$) and spectrum ($S_j^T$).
The time-resolved spectrum (\(D\)) such as FRTA signal is usually presented in a two dimensional matrix form \((m \times n)\), of which the column and row correspond to the time-dependent concentration and the corresponding spectral component, respectively. The FRTA signal \((D)\) can be expressed by the product of the time-dependent concentration \((C)\) and the spectral components \((S^T)\),

\[
D = C \cdot S^T
\]

where the columns of matrix \(C\), sized \(m \times k\), are the time-dependent concentrations of the \(k^{th}\) components at the time delay of \(m\) and the rows of matrix \(S^T\), sized \(k \times n\), are the corresponding \(k^{th}\) spectra measured as a function of wavelength \(n\). And \(m, k,\) and \(n\) are the time delay, the number of components, and the spectrum, respectively. In the global fitting analysis, the time-dependent concentrations \((C)\) were calculated by varying the rate constants \((k)\), the spectral components \((S^T)\) were extracted from the experimental FRTA signal, and the fitted FRTA signal \((D^{\text{fitted}})\) was obtained from \(C\) and \(S^T\) (i.e., \(D^{\text{fitted}} = C \cdot S^T\)). The best fitted FRTA signal was calculated by iteratively varying the rate constants in Eqns (S4)-(S6) until the difference between the experimental FRTA signal \((D^{\exp})\) and the fitted FRTA signal \((D^{\text{fitted}})\) was minimized, i.e.,

\[
\min \sum_{i,j} (D_{ij}^{\exp} - D_{ij}^{\text{fitted}})^2
\]  

(S7)
4. QM/MM calculations

The optimized molecular structures and electronic energies of two model PDAs were calculated at 20 and 80 °C by using the Gaussian 09W Package. Since PDAs were complicated molecular systems, the calculations were simplified by neglecting the terminal alkyl chains of two PDAs as shown in Figure S4. Furthermore, the multi-layered ONIOM (QM/MM) scheme with the DFT (b3lyp) and UFF methods was used for optimizing the molecular structures of model PDAs that contain 8 monomer units. After the optimization of the molecular structures, the electronic energies of model PDAs were calculated by using the DFT (b3lyp) and a STO-3G basis set. For model PCDA-PDA, carboxylic acid groups and ene-yne chain were quantum mechanically modeled and the alkyl chains between carboxylic acid groups and ene-yne chains were treated by classical molecular mechanics. For model Bis-PDA-Ph, p-phenylene groups and ene-yne chains were quantum mechanically modeled and the remaining alkyl chains were treated by classical molecular mechanics as shown in Figure S4. The optimized structures of two model PDAs are presented in Figures S5 and S6.
Figure S4. Multi-layered ONIOM (QM/MM) scheme to optimize the molecular structure of (A) model Bis-PDA-Ph and (B) model PCDA-PDA.
Figure S5. Optimized structure of model Bis-PDA-Ph at (A) 20 and (B) 80 °C.
Figure S6. Optimized structure of model PCDA-PDA at (A) 20 and (B) 80 °C.
Figure S7. Electronic energies of (A) model Bis-PDA-Ph and (B) model PCDA-PDA at 20 and 80 °C. The electronic energies near HOMO and LUMO levels and the corresponding molecular orbitals are shown as well.
5. NMR spectra

Figure S8. $^1$H NMR (300 MHz) of compound Bis-PCDA-Ph in CDCl$_3$. $\delta$ (ppm): 0.83-0.87 (t, $J = 6.9$ Hz, 6H), 1.23-1.53 (m, 52H), 1.68-1.73 (m, 9H), 1.69-1.76 (m, 4H), 2.20-2.24 (m, 8H), 2.50-2.55 (t, $J = 7.5$ Hz, 4H), 7.06 (s, 4H).
Figure S9. $^{13}$C NMR (300 MHz) of compound Bis-PCDA-Ph in CDCl$_3$. **δ** (ppm): 172.15, 148.05, 122.38, 77.44, 77.01, 76.59, 65.31, 34.31, 31.92, 29.65, 29.63, 29.61, 29.48, 29.35, 29.10, 29.08, 29.03, 28.90, 28.86, 28.75, 28.35, 28.29, 24.86, 22.63, 19.21, 19.19.
Figure S10. (A) IR spectra of model PCDA-PDA in Figure S6 at 20 and 80 °C obtained by the quantum chemical calculations. The frequency was calibrated by a correction factor of 0.931. (B) FTIR spectra measured with PCDA-PDA at 20 and 80 °C. The carbonyl peaks are shown. As the hydrogen-bonds are broken at 80 °C, the carbonyl peak is blue-shifted. The calculated IR spectra are in excellent agreement with the measured FTIR spectra.
References in the main text


References


