Electronic Supplementary Information

Photoresponsive AA/BB supramolecular polymers comprised of stiff-stilbene based guests and bispillar[5]arenes

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1. NMR and HR-ESI-MS spectra of compound Z-G, E-G and H.

Chart S1. The structure of compound Z-G.

Figure S1. $^1$H NMR spectrum of Z-G (CDCl$_3$, 400 MHz).

Figure S2. $^{13}$C NMR spectrum of Z-G (CDCl$_3$, 100 MHz).
Figure S3. HR-ESI-MS spectrum of Z-G.

Chart S2. The structure of compound E-G.

The integral area of the Z-G proton signal (7.78 ppm) in $^1$H NMR spectra is only about 3% of the integral area of E-G proton signal, which revealed the almost complete conversion.\cite{1}
Figure S4. $^1$H NMR spectrum of \textit{E-G} (CDCl$_3$, 400 MHz).

Chart S3. The structure of compound \textit{H}.

Figure S5. $^1$H NMR spectrum of \textit{H} (CDCl$_3$, 400 MHz).
2. Absorption and emission spectra of $Z$-G and $E$-G.

Figure S6. The UV-vis spectra of $Z$-G and $E$-G in CH$_2$Cl$_2$ (1.0×10$^{-5}$ mol/L).

Figure S7. The fluorescence spectra of $Z$-G and $E$-G in CH$_2$Cl$_2$ (1.0×10$^{-5}$ mol/L, $\lambda_{ex} = 340$ nm).
3. COSY spectra of Z-G + H and E-G + H at 150 mM.

Figure S8. COSY spectrum of a chloroform-d solution of 150 mM Z-G + H.

Figure S9. COSY spectrum of a chloroform-d solution of 150 mM E-G + H.
4. ROESY spectra of Z-G + H and E-G + H at 150 mM.

Figure S10. ROESY spectrum of a chloroform-d solution of 150 mM Z-G + H.

Figure S11. ROESY spectrum of a chloroform-d solution of 150 mM E-G + H.
5. DOSY spectra of Z-G + H and E-G + H at 5-150 mM.
Figure S12. DOSY spectra of Z-G + H at 5, 20, 40, 70, 100, 150 mM in CDCl$_3$. (from $^1$H NMR spectroscopy 600 MHz, CDCl$_3$, 298 K).
Figure S13. DOSY spectra of \( E \cdot G + H \) at 5, 20, 40, 70, 100, 150 mM in CDCl\(_3\). (from \(^1\)H NMR spectroscopy 600 MHz, CDCl\(_3\), 298 K).

The observation of a sharp decrease in the diffusion coefficient upon increasing concentration of 1:1 mixture of \( E \cdot G + H \) suggested the formation of linear polymers.\(^2\)

We also estimate the average degree of polymerization (DP) of supramolecular polymers at 150 mM roughly from DOSY experiments using following equation:

\[
DP = (D_A/D)^3
\]
where \( D_A \) is the average diffusion coefficient for the AA and BB monomer \((3.97 \times 10^{-10} \text{ m}^2\text{s}^{-1} \text{ at 150 mM})\), \( D \) is the diffusion coefficient for the sample of supramolecular polymer measured by DOSY \((3.83 \times 10^{-11} \text{ m}^2\text{s}^{-1} \text{ at 150 mM})\). The average degree of polymerization was calculated to be 1110. We realized that this is a very rough estimation.\(^3\)

6. Schematic illustration of assembly of 1:1 mixture of \( E-G + H \) at < 12 mM.

Figure S14. Schematic illustration of assembly of 1:1 mixture of \( E-G + H \) at < 12 mM.
7. DLS experiments

Figure S15. The diameter of supramolecular polymers from 1:1 mixture of E-G and H at 50 mM determined from DLS.

8. Assembly/disassembly behaviour of the AA/BB supramolecular polymers (20 mM) by photo irradiation.
Figure S16. (a) The DOSY spectrum of 1:1 mixture of Z-G + H at 20 mM. (b) The DOSY spectrum of the mixture after irradiation by 387 nm light. (c) The DOSY spectrum of the mixture from (b) after irradiation by 360 nm light. (600 MHz, CDCl₃, 298 K).

The diffusion constant (D) of the 20 mM mixture of Z-G and H was \((3.57 \pm 0.07) \times 10^{-10}\) m²s⁻¹. After irradiation by 387 nm light for 80 min, the diffusion constant (D) of the mixture was determined to be \((2.83 \pm 0.12) \times 10^{-10}\) m²s⁻¹. The decreasing diffusion constant (D) indicated the possible formation of polymers due to the transformation from Z-G to E-G by photo-irradiation. The reverse isomerization was achieved by irradiation at > 360 nm. The diffusion constant (D) of the mixture was increased to \((3.15 \pm 0.07) \times 10^{-10}\) m²s⁻¹. The changing of D in the mixture of Z-G + H before and after irradiation by 387 nm and then 360 nm at 20 mM has similar trend with those at 100 mM.
9. **Z/E isomerization ratio at different irradiation time.**

Figure S17. (a) The percentage of $E$-$P$ upon irradiation of Z-P (20 mM) for 0 min, 20 min, 40 min, 60 min and 80 min. (b) The percentage of $E$-$P$ when irradiation of Z-P (100 mM) for 0 min, 60 min, 140 min, 250 min, 270 min and 300 min.

We determined the Z/E isomerization ratio by $^1$H NMR at different irradiation time at 20 mM. The percentage of $E$-$P$ is increasing upon irradiation of Z-P at 387 nm. The percentage of $E$-$P$ is 97% at photostationary state. We also determined the Z/E isomerization ratio by $^1$H NMR at different irradiation time at 100 mM. The photoisomerization reaction reached its photostationary state with 95% of $E$-$P$ after irradiating Z-P for 4.5 h.
10. UV spectra of 1:1 mixture of Z-G + H at 100 mM.

Figure S18. The UV-vis spectra of 1:1 mixture of Z-G + H at 100 mM in CHCl$_3$ after stay for 0 h and 4.5 h under dark.

11. References.

