Supporting Information

Single-molecule fluorescence dynamics of butadiyne-linked porphyrin dimer: Effect of conformational flexibility in host polymers

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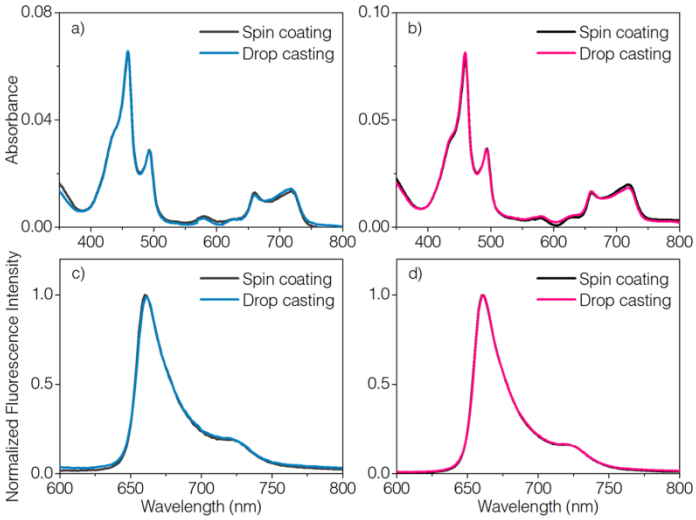

Figure S1. Absorption (a, b) and fluorescence (c, d) spectra of **Z2B** in 50 mg/ml PMMA polymer matrix to confirm the same conditions that the films produced by spin-coating and drop-casting methods. We dropped several blobs of toluene (a, c) and chloroform (b, d) solutions of **Z2B** (10^{-3}–10^{-5} M) containing PMMA with the concentration of 50 mg/ml on rigorously cleaned quartz cover slides. The spin-coated film was produced by spin-coating at 400 rpm, and the drop-cast film was dried for 2 hours in a chamber. The absorption spectra of **Z2B** in 50 mg/ml PMMA polymer matrix show the same features regardless of the spin-coating and drop-casting methods (a, b). In the same manner, the fluorescence spectra of **Z2B** in 50 mg/ml PMMA polymer matrix display the peak with the same ratio at 660 nm (c, d). In fact, changing the sample preparation conditions from spin-coating to drop-casting has no observable effect on the single molecule behaviors of molecular systems.[1]

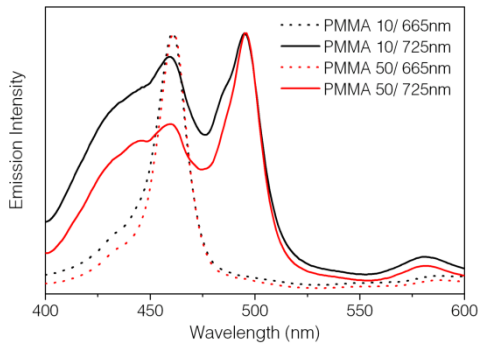

Figure S2. Fluorescence excitation spectra of **Z2B** in 10 and 50 mg/ml PMMA polymer matrices (detection wavelengths: 665 and 725 nm). Fluorescence excitation spectra in polymer matrix do not reproduce the absorption spectra. A difference at 460 nm (725 nm detection) indicates that the conformational change of **Z2B** is affected by the molecular surroundings.

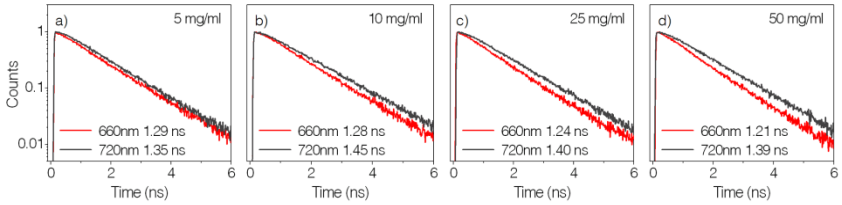

Figure S3. Time-resolved fluorescence decays in bulk PMMA film measured by using TCSPC method. In the ensemble measurement, the fluorescence lifetimes of **Z2B** in twisted form at 660 nm (5 mg/ml: 1.29 ns, 10 mg/ml: 1.28 ns, 25 mg/ml: 1.24 ns, 50 mg/ml: 1.21 ns) are relatively shorter than those in planar form at 720 nm (5 mg/ml: 1.35 ns, 10 mg/ml: 1.45 ns, 25 mg/ml: 1.40 ns, 50 mg/ml: 1.39 ns) regardless of the PMMA polymer density.

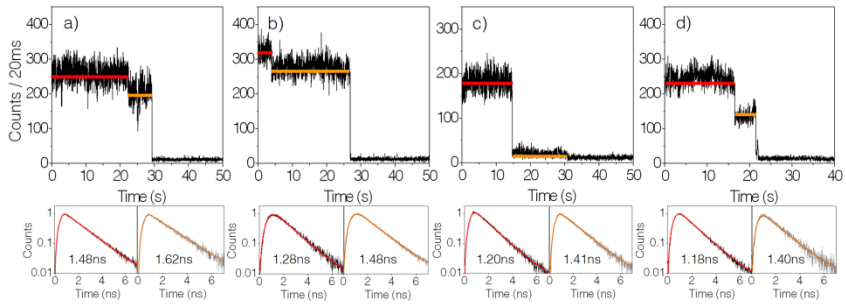

Figure S4. Two-step photobleaching behaviors in the FITs of **Z2B** depending on the density of the polymer matrix. (a) 5, (b) 10, (c) 25, and (d) 50 mg/ml PMMA matrix. The FITs were recorded using an excitation wavelength of 450 nm. Figures under the FITs present fluorescence decay profiles corresponding to the first emissive level (red) and second level (orange) in the FITs, which were fitted with a single exponential decay function.

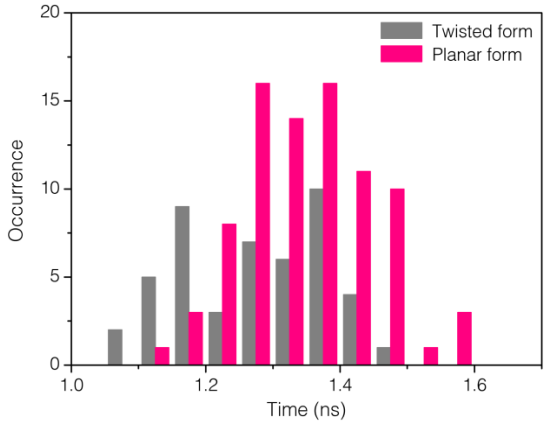

Figure S5. Fluorescence lifetime distributions of **Z2B** in 50 mg/ml PMMA polymer matrix. The fluorescence lifetimes of single molecules were obtained by fitting all the photons in the first emissive level in the FITs. The average fluorescence lifetime of 1.27 ns (gray) by the twisted form is shorter than 1.34 ns (pink) of the planar form. This feature illustrates that the fluorescence lifetime of the twisted conformer is largely shorter than that of the planar conformer.

References

1. S. S. Sartori, S. D. Feyter, J. Hofkens, M. Van der Auweraer and F. C. De Schryver, *Macromolecules*, 2003, **36**, 500–507.