Supplementary Information for

Single molecule spectroscopic investigation on various multiporphyrin systems as a molecular photonic device

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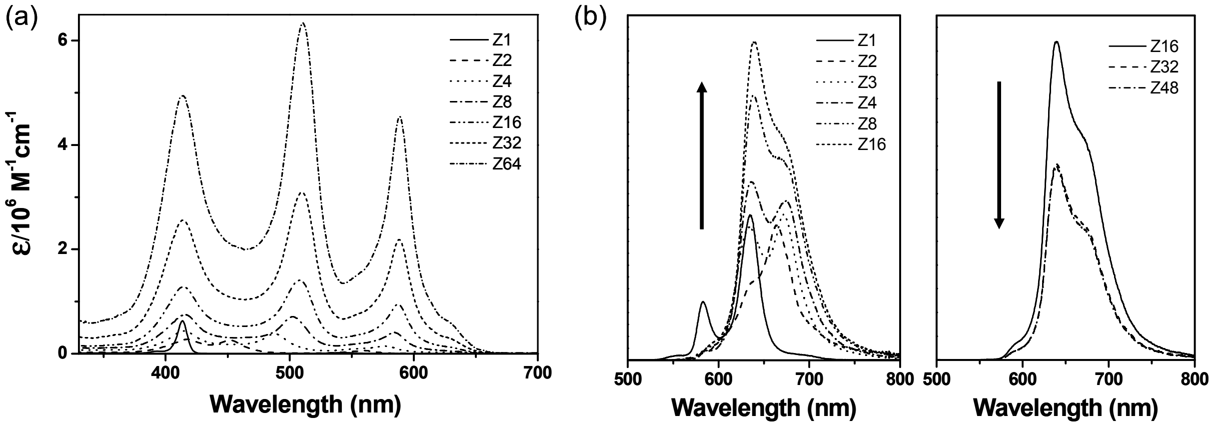

Fig. S1 Molar extinction coefficient spectra (a) and steady-state fluorescence spectra (b) of *meso*-*meso* directly linked linear porphyrin arrays ($\boldsymbol{Z_{n+2}}$).

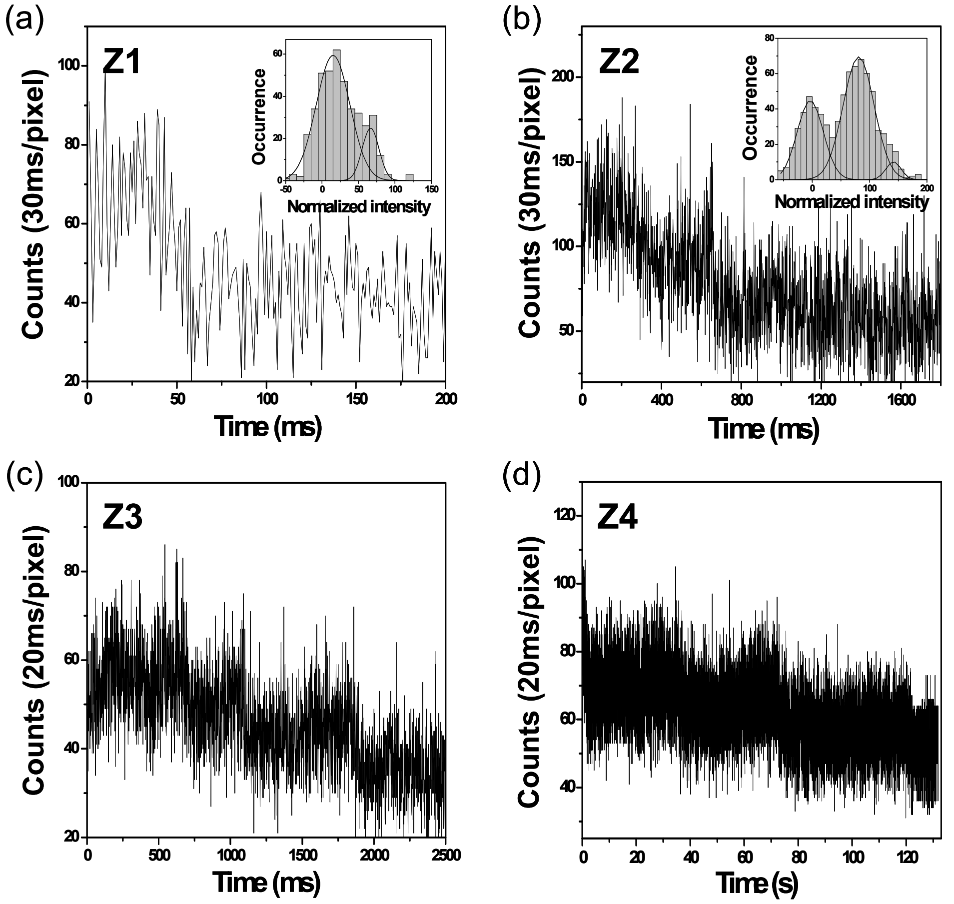

Fig. S2 Fluorescence intensity trajectories of **Z1** (a), **Z2** (b), **Z3** (c), and **Z4** (d). The insets in (a) and (b) represent the histograms of the fluorescence intensities corresponding to each fluorescence intensity trajectory.

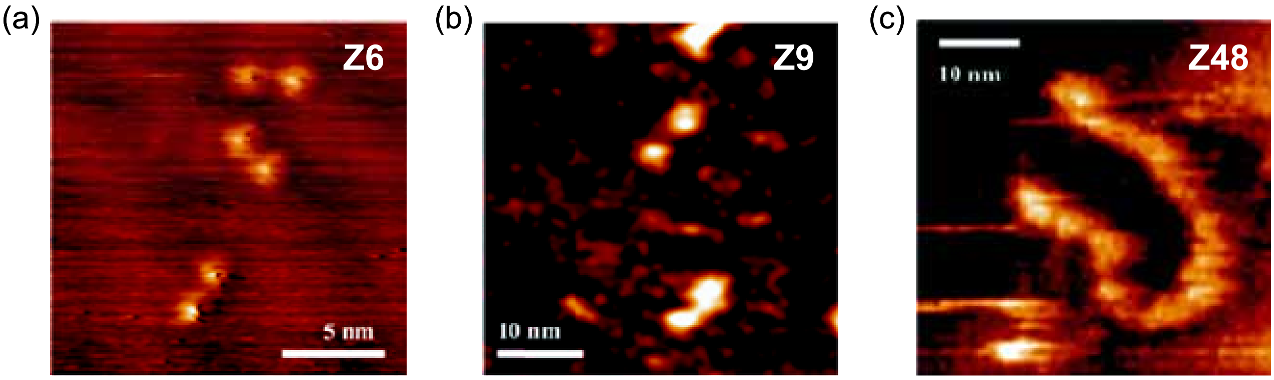

Fig. S3 The STM images of **Z6** (a), **Z9** (b), and **Z48** (c). **Z6** shows a pair of images that are nearly constantly spaced at a distance of 55 Å. As bright images usually come from strong adsorption of π-conjugated molecules on a metal surface, the bright pair-based images obtained here can be assigned to the adsorption of the two end porphyrins with their planes parallel to the metal substrate. **Z9**, being similar to **Z6**, seems to take a bent conformation with the porphyrin intermediates between the two end porphyrins being detached from the metal surface. This assignment suggests conformational flexibility in the longer arrays, which is highlighted in **Z48.** The STM image of **Z48** displays a severely bent structure on the metal surface. Importantly, the molecular length of **Z48** is estimated to be 43.5 nm from this STM image, which is exactly its predicted value.

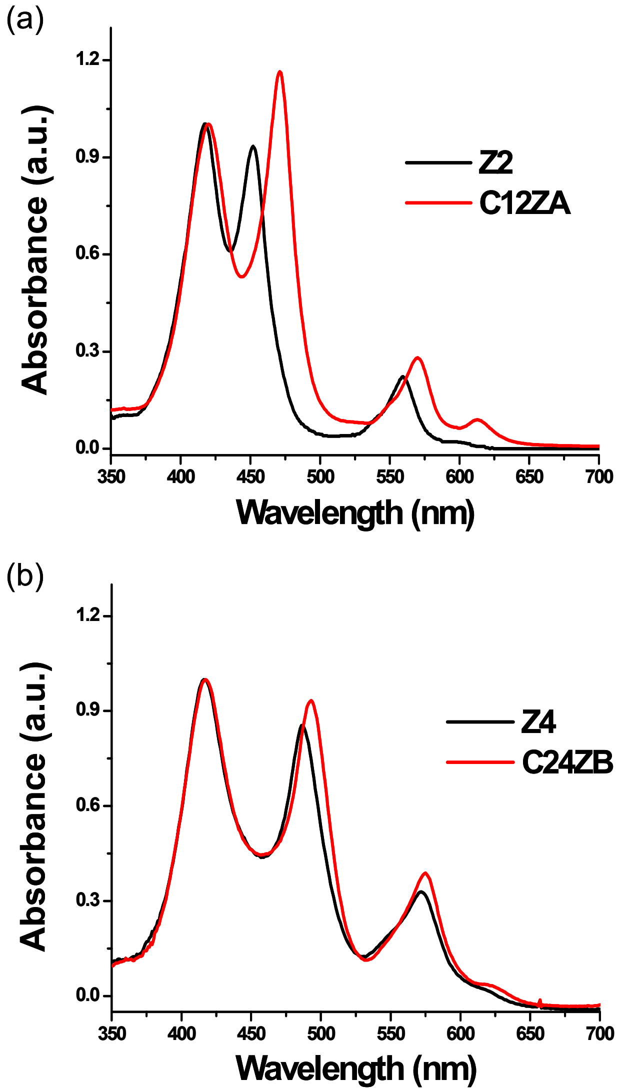

Fig. S4 Steady-state absorption spectra of **Z2** and dodecameric cyclic porphyrin array **C12ZA** (a) and those of **Z4** and tetracosameric cyclic porphyrin array **C24ZB** (b). The spectral red shift in the absorption spectrum of **C12ZA** compared to that of **Z2** clearly shows the signature of strong coupling between **Z2** subunits. On the other hand, the absorption spectrum of **C24ZB** resembles to that of **Z4**. The strong dipole-dipole coupling in **C12ZA** is believed to arise from the short interchromophoric distance between diporphyrin subunits despite weaker transition dipole strength in **Z2** than that in **Z4**.

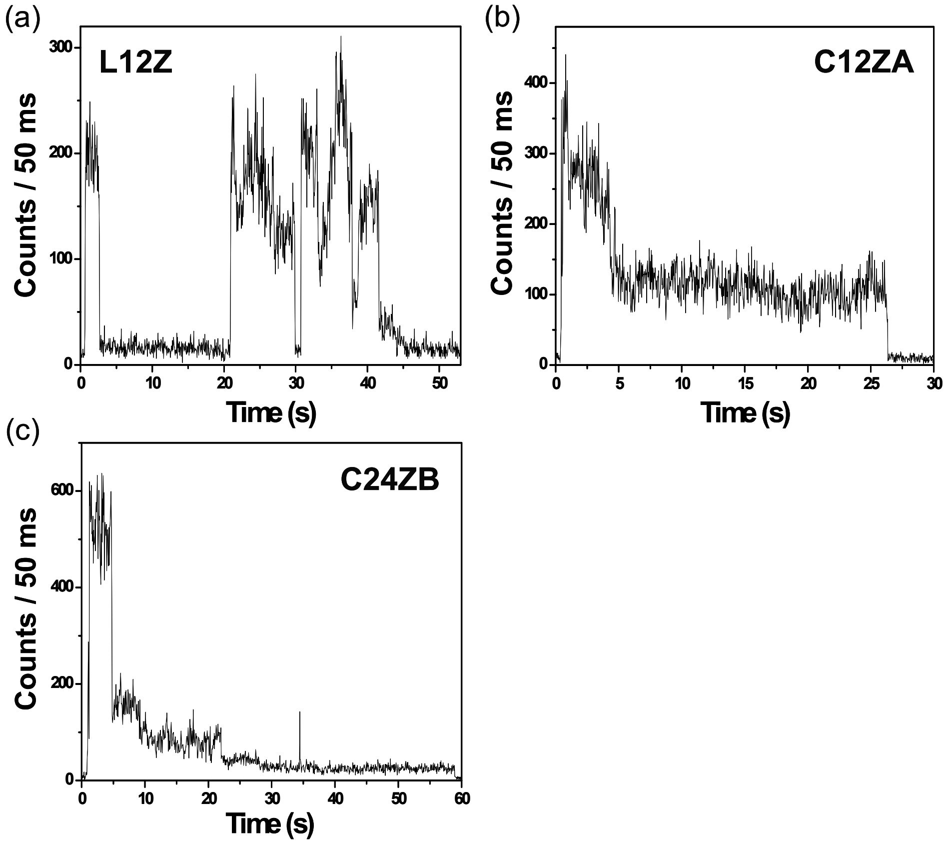

Fig. S5 Fluorescence intensity trajectories of 1,3-phenylene-bridged linear porphyrin array **L12Z** (a), cyclic arrays **C12ZA** (b) and **C24ZB** (c).

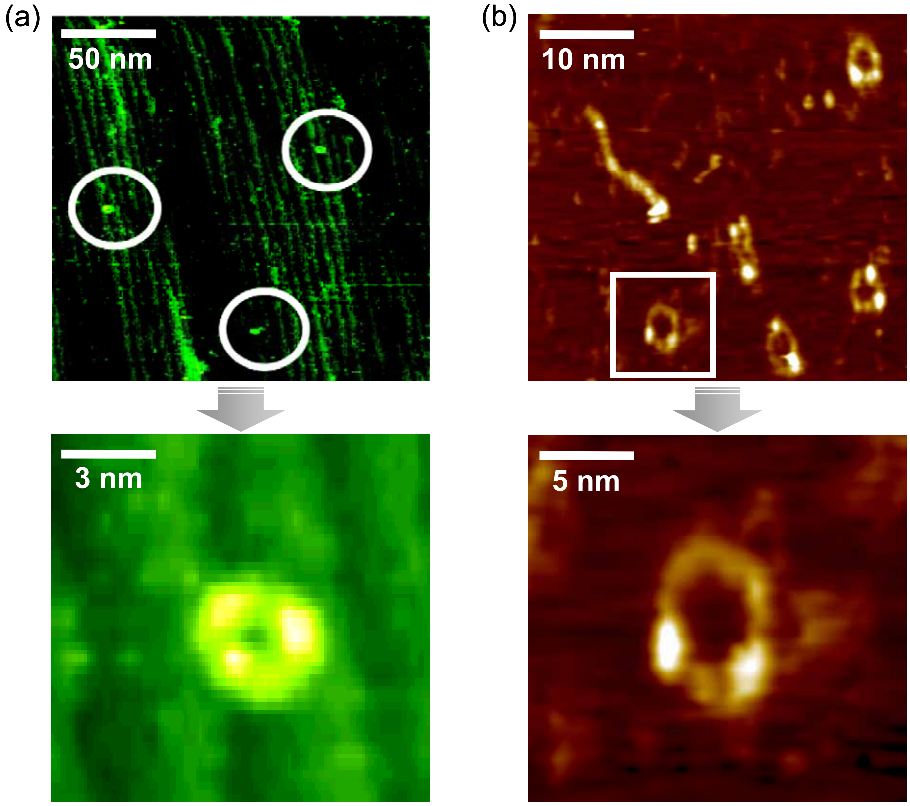

Fig. S6 The STM images of **C12ZA** (a) and **C24ZB** (b) exhibit wheel-like structures. An average height of the STM images of **C12ZA** estimated on the basis of the height histogram is ca. 2.9 ± 1.2 Å and an average diameter is 35.0 ± 6.7 Å, being similar to a calculated diameter of ca. 36-38 Å. The average diameter of the STM images of **C24ZB** is 45-70 Å, which matches roughly with its calculated diameter (ca. 70 Å). **C24ZB** shows deformed images, indicating the conformational flexibility.

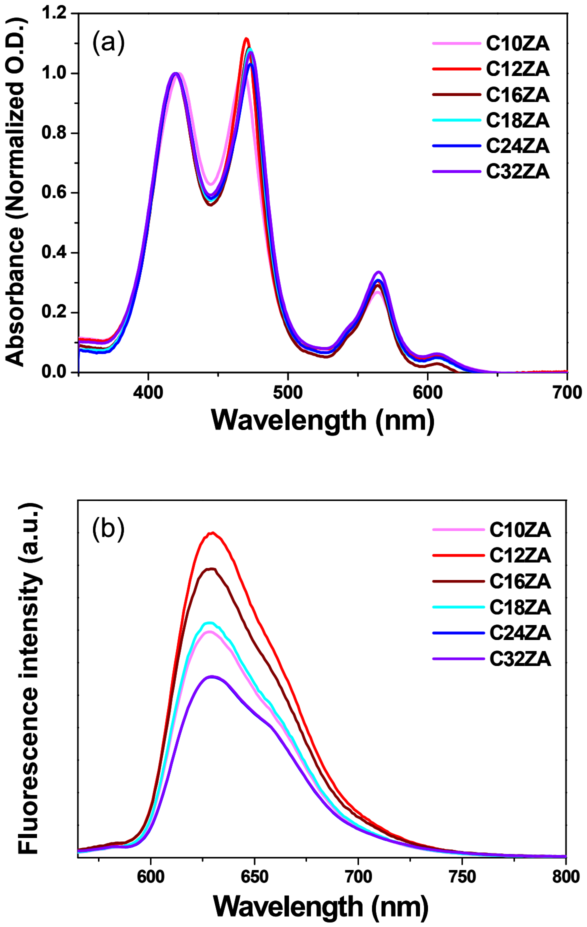

Fig. S7 Steady-state absorption and fluorescence spectra of cyclic porphyrin arrays **C10ZA**, **C12ZA**, **C16ZA**, **C18ZA**, **C24ZA**, and **C32ZA** in toluene. The little change in positions of the Q-bands in the absorption spectra and similar spectral shapes of the fluorescence spectra indicate that electronic coupling energies are similar for all the cyclic porphyrin arrays, which infer that angles between adjacent diporphyrin subunits are maintained approximately as 120° although cyclic porphyrin array becomes larger.

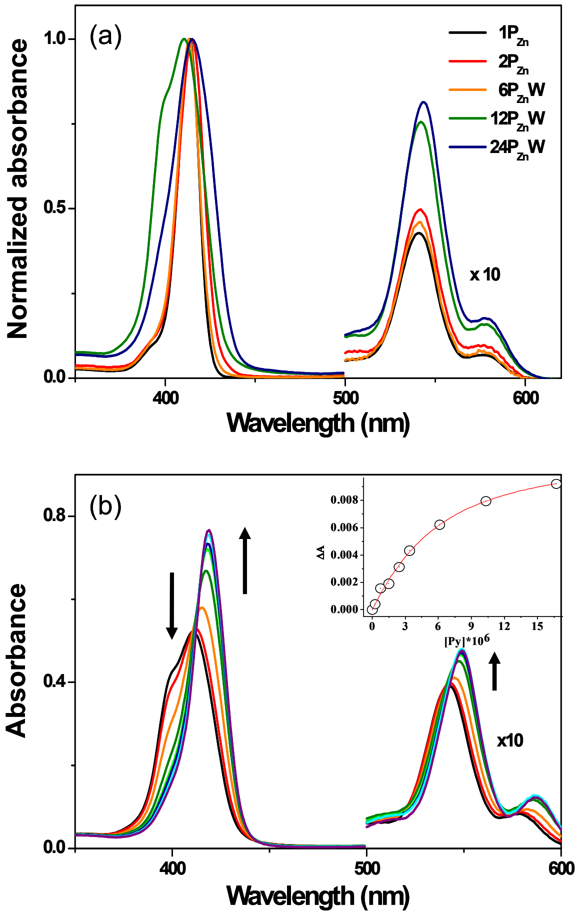

Fig. S8 Steady-state absorption spectra of zinc(II) porphyrin dendrimers ($\mathbf{6P_{Zn}W}$, $\mathbf{12P_{Zn}W}$, and $\mathbf{24P_{Zn}W}$) and dendrons ($\mathbf{1P_{Zn}}$ and $\mathbf{2P_{Zn}}$) in chloroform (a) and spectroscopic titration spectra of $\mathbf{12P_{Zn}W}$ with $\mathbf{C_6Py_2}$ (0 → 300 equiv.) (b). The inset shows the absorbance change as the guest concentration increases and the fitted line as an association constant equation. The concentration of $\mathbf{12P_{Zn}W}$ of 2.90 x 10^{-9} M and the monitoring wavelength of 419 nm were used for the titration experiments. [Py] is the total number of binding sites of $\mathbf{C_6Py_2}$, which was calculated as 2 times the concentration of $\mathbf{C_6Py_2}$.