Electronic Supporting Information for

Control of the Conformational Dynamics of *meso-meso* Vinylene-bridged Zn(II) Porphyrin Dimers through Diamine Coordination

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3. References

1. Experimental Details

Sample Preparation. The details in synthesis, characterization, and X-ray crystallographic analysis of **1** and **2** are described elsewhere.[1] The X-ray crystallographic data were originally obtained for the Ni(II) porphyrin dimers with the same structures.[1] They were taken at –180 °C with a Rigaku RAXIS-RAPID diffraction by using graphite monochromated Cu-Kα radiation (λ = 1.54187 Å). The structures were solved by direct method. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Zinc-copper couple for McMurry coupling was purchased from Sigma-Aldrich. All α,ω-diaminoalkanes used here were purchased from Sigma-Aldrich and dissolved in toluene without further purification. The coordinated samples were passed through membrane filters before all measurements to prevent light scattering from remaining ligand particles.

Steady-State Absorption and Fluorescence Emission. Steady-state UV-Vis absorption spectra were recorded on a commercial spectrometer (Cary5000, Varian). For the observation of steady-state emission spectra in the near-infrared (NIR) region, a photomultiplier tube (R5108, Hamamatsu), a lock-in amplifier (5210, EG&G) combined with a chopper and a CW He-Cd laser (Omnichrome 74, Melles Griot) for the 442 nm excitation were used. All steady-state measurements were carried out by using a quartz cuvette with a path length of 1 cm at ambient temperatures.

Temperature Dependence Experiments. For the temperature-dependent steady-state and time-resolved absorption and emission studies, a temperature-controlled liquid nitrogen cryostat (Optistat DN, Oxford Instruments) was used. The temperatures were maintained to within ±0.05 K and allowed to equilibrate for 30 minutes before spectroscopic measurements. The results were controlled by comparison with measurements in a regular cuvette at room temperature, as possible.

Picosecond Time-resolved Fluorescence. Time-resolved fluorescence decays were obtained by using a time-correlated single photon counting (TCSPC) technique. A mode-locked Ti:sapphire oscillator (MaiTai-BB, SpectraPhysics) was used as the excitation light source, which provides a fwhm (full width at half maximum) of 80 fs with a high repetition rate of 80 MHz. In order to minimize artifacts such as thermal lensing and accumulation effect, the repetition rate was reduced down to 800 kHz using a home-made acousto-optic pulse selector. The picked fundamental pulses were frequency-doubled by a BBO nonlinear crystal (Eksma) of 1 mm thickness. The fluorescence was collected by a microchannel plate photomultiplier (MCP-PMT, R3809U-51, Hamamatsu) with a thermoelectric cooler (C4878, Hamamatsu). Time-resolved fluorescence signals were calculated by a TCSPC board (SPC-130, Becker & Hickel

GmbH). The overall instrumental response function (IRF) was determined to be less than 30 ps (fwhm) in all spectral regions. The polarization of the photoexcitation pulses was set to be vertical to the laboratory frame by both a half-wave retarder and a Glan laser polarizer and sheet polarizers were used in the fluorescence collection path at magic angle (54.7°) to obtain polarization-independent population decays.

Femtosecond Transient Absorption. The femtosecond time-resolved transient absorption (fs-TA) spectrometer consisted of an OPA (Optical Parametric Amplifier; Palitra, Quantronix) pumped by a Ti:sapphire regenerative amplifier system (Integra-C, Quantronix) operating at 1 kHz repetition rate and an optical detection system. The generated OPA pulses had a pulse width of ~ 100 fs and an average power of 100 mW in the range 280-2700 nm which were used as pump pulses. White light continuum (WLC) probe pulses were generated using a sapphire window (3 mm of thickness) by focusing of small portion of the fundamental 800 nm pulses which was picked off by a quartz plate before entering to the OPA. The time delay between pump and probe beams was carefully controlled by making the pump beam travel along a variable optical delay (ILS250, Newport). Intensities of the spectrally dispersed WLC probe pulses are monitored by a High Speed spectrometer (Ultrafast Systems) for both visible and near-infrared measurements. To obtain the time-resolved transient absorption difference signal (DA) at a specific time, the pump pulses were chopped at 500 Hz and absorption spectra intensities were saved alternately with or without pump pulse. Typically, 4000 pulses excite samples to obtain the fs-TA spectra at a particular delay time. The polarization angle between pump and probe beam was set at the magic angle (54.7°) using a Glan-laser polarizer with a half-wave retarder in order to prevent polarization-dependent signals. Cross-correlation *fwhm* in pump-probe experiments was less than 200 fs and chirp of WLC probe pulses was measured to be 800 fs in the 400-800 nm region. To minimize chirp, all reflection optics in the probe beam path and the 2 mm path length of quartz cell were used. After the fluorescence and fs-TA experiments, we carefully checked absorption spectra of all compounds to detect if there were artifacts due to degradation and photo-oxidation of samples. HPLC grade solvents were used in all steady-state and time-resolved spectroscopic studies. The three-dimensional data sets of ΔA versus time and wavelength were subjected to singular value decomposition and global fitting to obtain the kinetic time constants and their associated spectra using Surface Xplorer software (Ultrafast Systems).

2. Supporting Information

Table S1. Decay parameters measured by time-correlated single photon counting (TCSPC) in toluene, paraffin oil, and 2-MeTHF at different temperatures.[a,b]

	Medium	$\Phi_{\mathrm{fl}}{}^{c}$	$\lambda_{\mathrm{em}}{}^{d}$ / nm	τ_1 / ps	τ_2 / ps
1	Toluene	0.06	670	30 (96.5)	870 (3.5)
			820	35 (-17.8)	1000 (82.2)
	Paraffin oil	0.02	620	300 (40.5)	1100 (59.5)
			780	330 (35.3)	1200(64.7)
	2-MeTHF (77K)	-[e]	720	1500 (100)	-
			800	1400 (100)	-
	2-MeTHF (297K)	-[e]	720	30 (94.8)	770 (5.2)
			800	30 (-47.4)	710 (53.6)
2	Toluene	0.02	710	45 (95.2)	550 (4.8)
			840	45 (-34.7)	550 (65.3)
	Paraffin oil	0.03	650	150 (24.6)	780 (75.4)
			800	150 (28.5)	900 (71.5)
	2-MeTHF (77K)	-[e]	730	1400 (100)	-
			820	1300 (100)	-
	2-MeTHF (297K)	-[e]	730	40 (92.5)	550 (7.5)
			820	40 (-25.9)	550 (74.1)

[a] The values in the parentheses represent the normalized pre-exponential factors.

[b] Negative amplitude values indicate rise profiles.

[c] Fluorescence quantum yields measured by using H_2TPP (in toluene, $\Phi_{\mathrm{fl}} = 0.11$ at 514 nm).

[d] The wavelength used for monitoring the time-resolved fluorescence.

[e] Not determined.

Table S2. List of parameters measured in steady-state absorption and fluorescence emission spectra in toluene, paraffin oil (at room temperature) and in 2-MeTHF (77 K) for **1**, **2**, and **1-*n*DA** and **2-*n*DA** series.

	Medium	λ_{abs}[a] (nm)	λ_{em}[b] (nm)	Stokes shift (cm^{-1})
1	Toluene	424, 475, 559, 637	782	2711
	Paraffin oil	431, 470, 555, 625	676	1533
	2-MeTHF (77K)	411, 484, 555, 681	704, 776 (sh.[c])	480
	1-3DA	436, 485, 567, 672	820	2686
	1-4DA	436, 485, 567, 673	820	2664
	1-5DA	433, 485, 568, 671	820	2708
	1-6DA	420, 490, 561, 671	820	2708
	1-7DA	421, 492, 562, 733	848	1850
	1-8DA	420, 490, 563, 704	828	2127
	1-9DA	431, 486, 562, 683	812	2326
	1-10DA	433, 485, 569, 669	793	2337
	1-12DA	433, 483, 568, 660	782	2364
2	Toluene	413, 486, 558, 668	790	2312
	Paraffin oil	410, 483, 555, 658	693	768
	2-MeTHF (77K)	417, 494, 508, 574, 709, 801 (sh.), 894	736, 774, 926	517[d], 387[e]
	2-3DA	422, 494, 570, 704	835	2229
	2-4DA	421, 494, 566, 703	837	2277
	2-5DA	432, 511, 584, 825 (sh.), 923	833	-[f]
	2-6DA	424, 502, 572, 796, 901	864	-[f]
	2-7DA	420, 499, 565, 771, 832 (sh.)	854	1261
	2-8DA	418, 498, 565, 753	848	1488
	2-9DA	419, 495, 564, 726	818	1549
	2-10DA	422, 494, 566, 698	798	1795
	2-12DA	421, 492, 566, 689	832	2495

[a] Peak maxima in the steady-state absorption spectra.

[b] Peak maxima in the steady-state fluorescence emission spectra.

[c] Shoulder peaks.

[d] Calculated by using λ_{abs} = 709 nm and λ_{emi} = 736 nm.

[e] Calculated by using λ_{abs} = 894 nm and λ_{emi} = 926 nm

[f] Not determined.

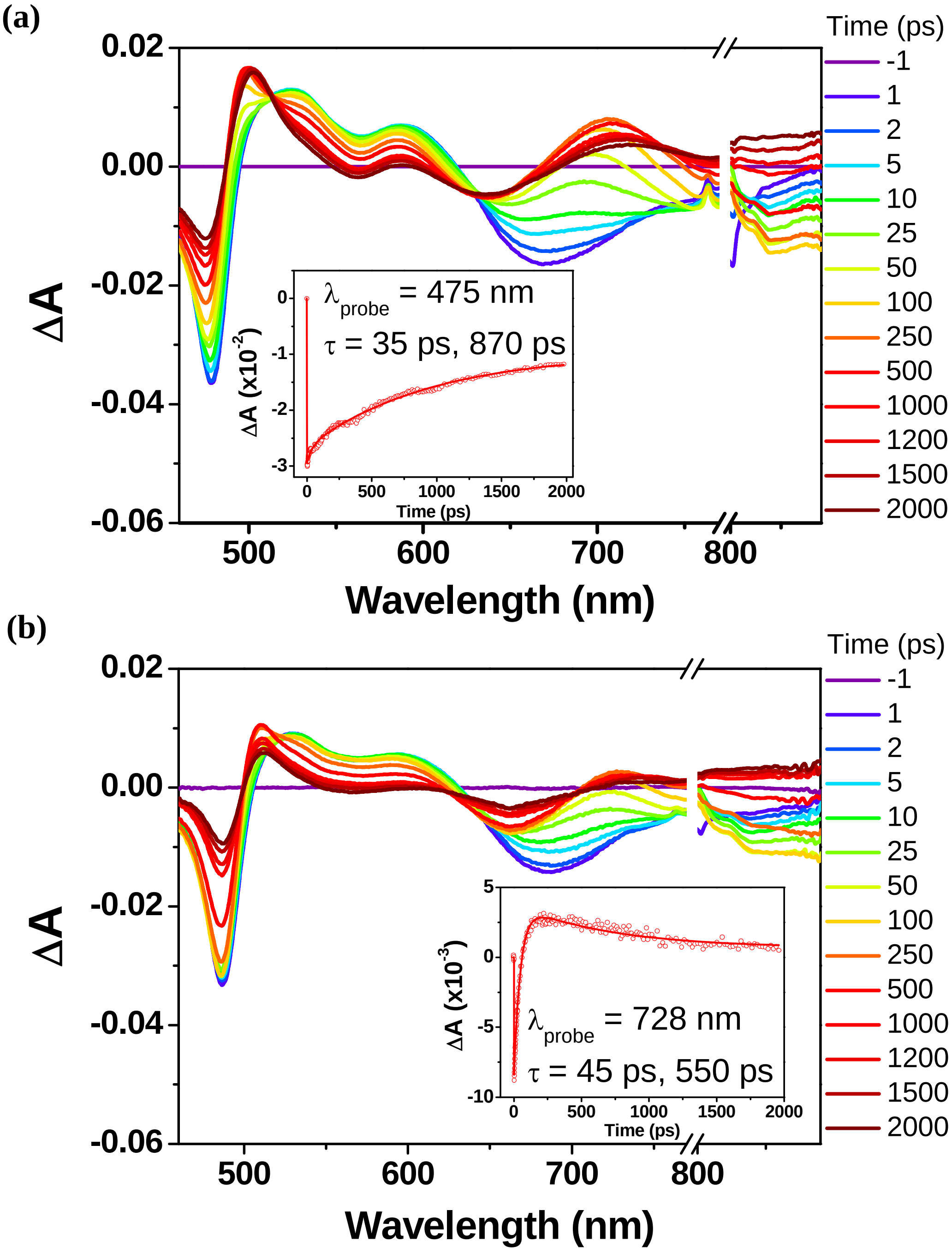


Fig. S1 Femtosecond transient absorption (TA) spectra and fitted decay profiles (insets) of (a) **1** and (b) **2** measured in toluene at room temperature. The excitation wavelength used was 660 nm.

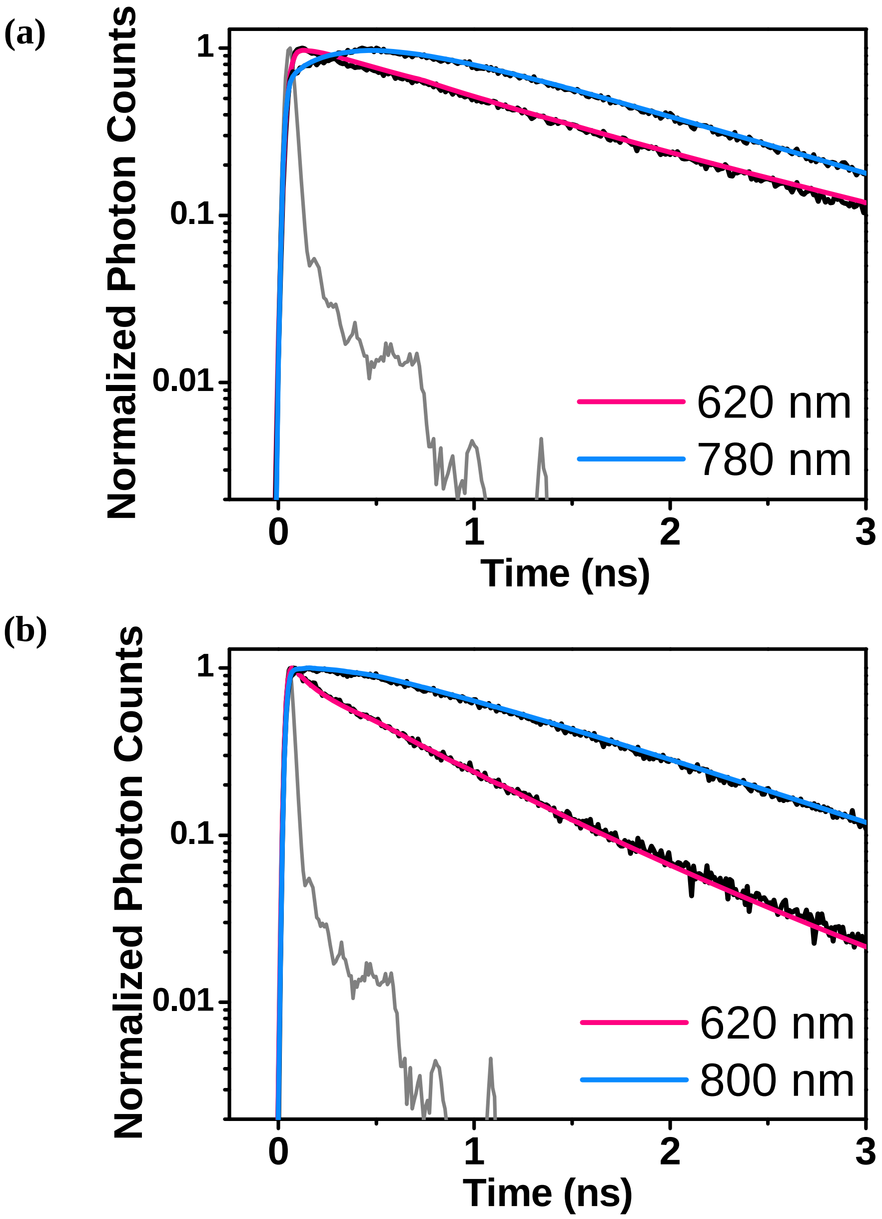


Fig. S2 Time-resolved fluorescence decay profiles of (a) **1** and (b) **2** measured in paraffin oil upon photoexcitation at 470 nm. The emission wavelengths monitored are indicated in the figures and the instrumental response function is represented by the gray trace.

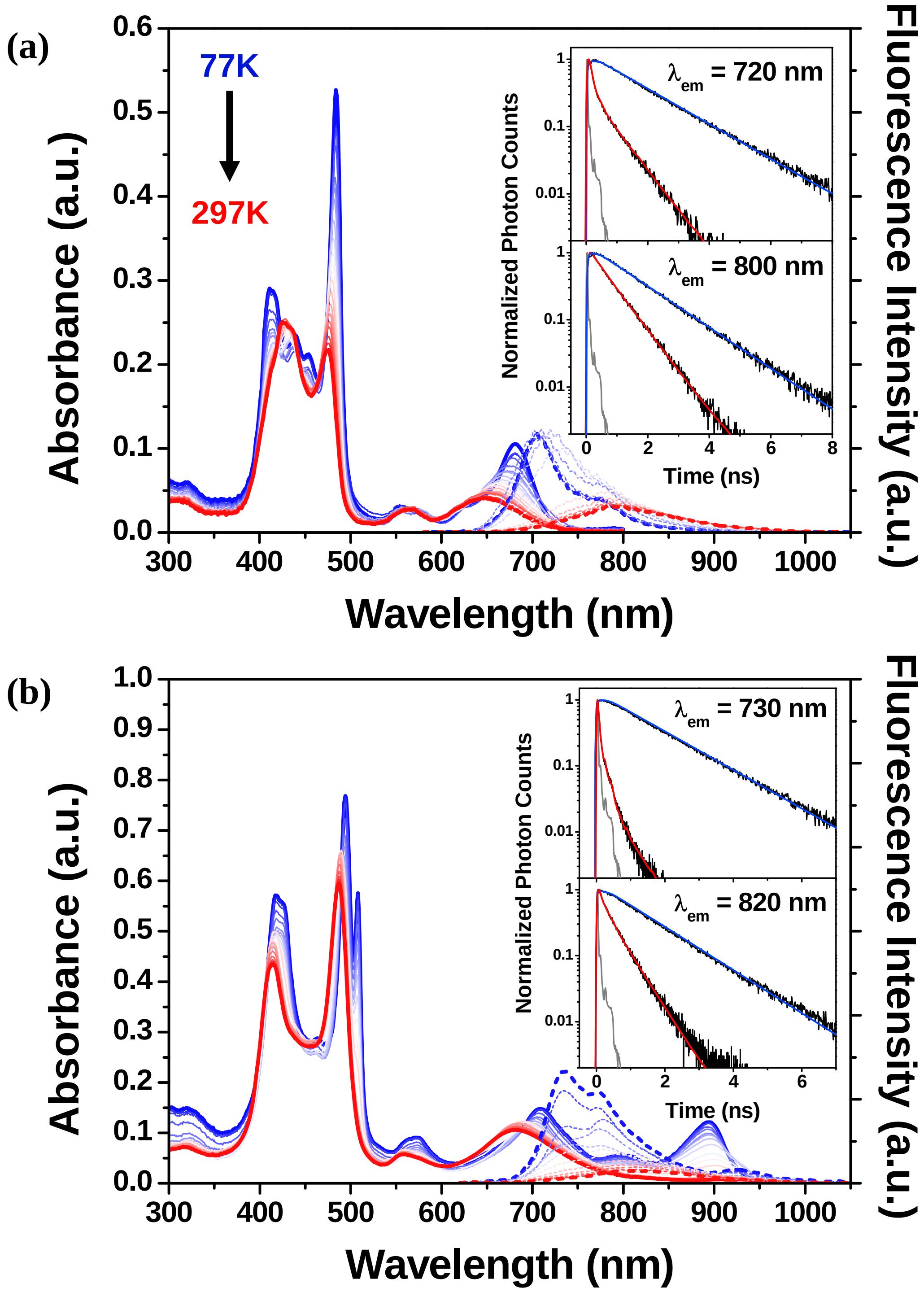


Fig. S3 Temperature-dependent steady-state absorption and fluorescence emission spectra of (a) **1** and (b) **2** measured in 2-MeTHF in the temperature range of 77 to 297 K. Insets show the fluorescence decay profiles (λ_{exc} = 470 nm) measured at the indicated wavelengths at 77 (blue) and 297 K (red), respectively.

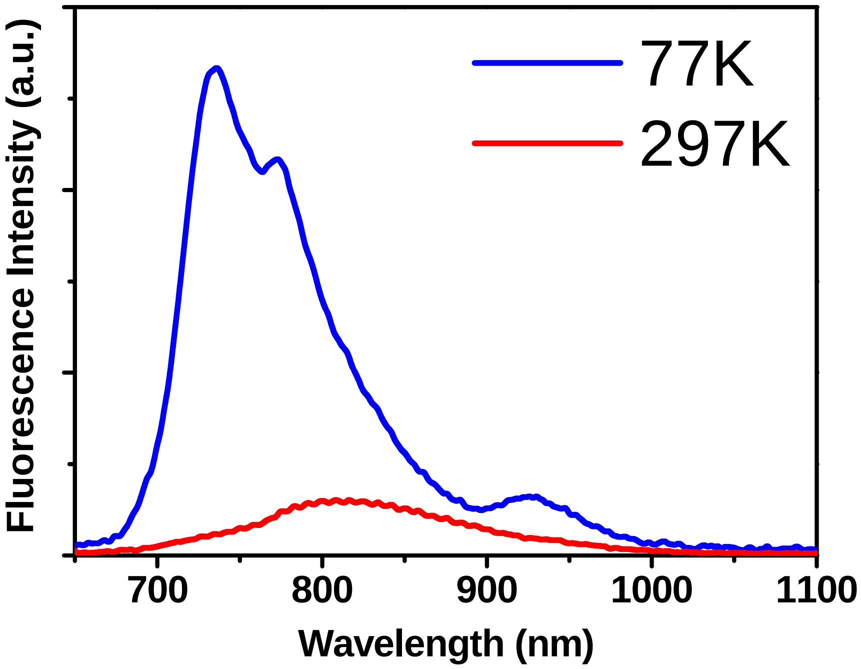
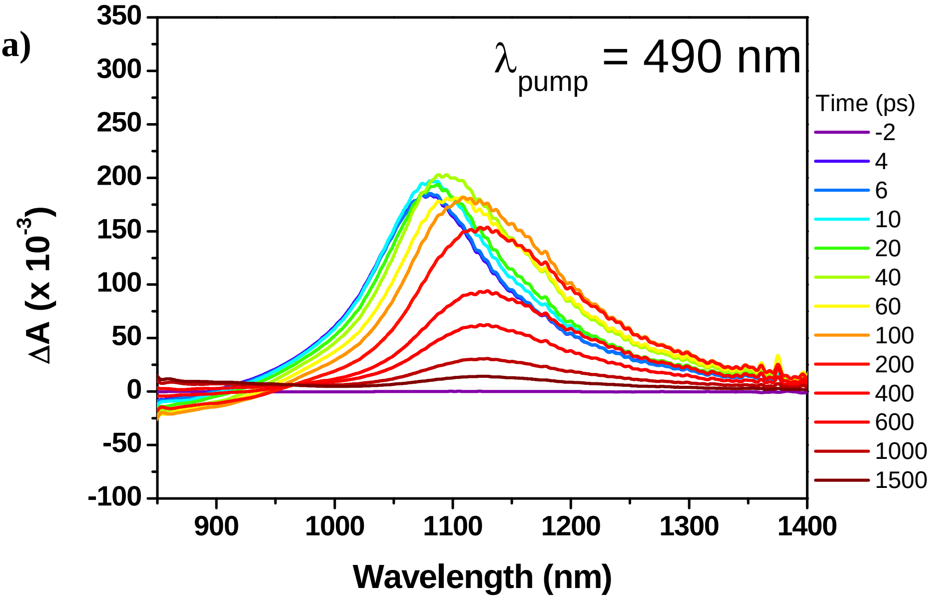


Fig. S4 Enlarged steady-state fluorescence emission spectra of **2** measured in 2-MeTHF at 77 (blue) and 297 K (red).

(a)



(b)

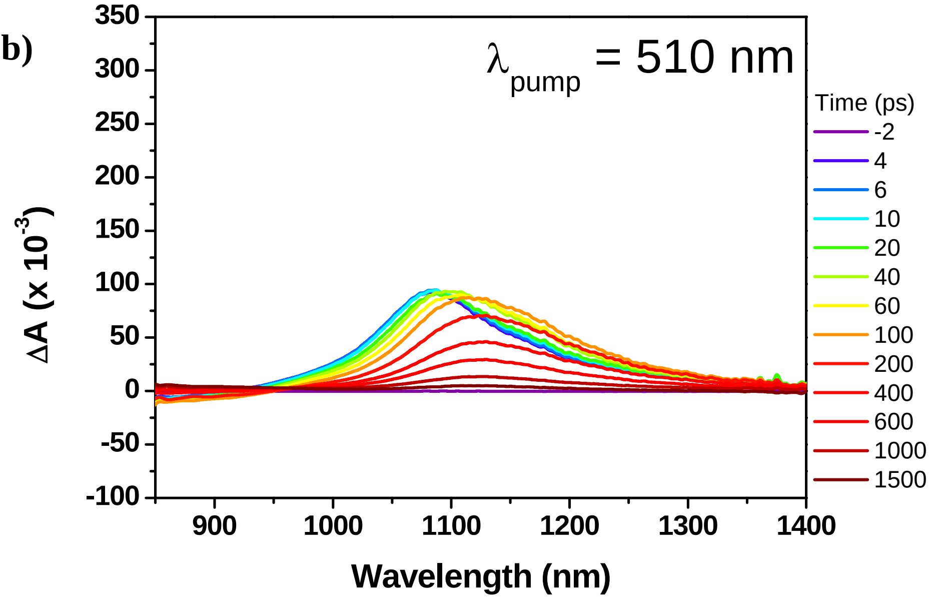


Fig. S5 Near-infrared transient absorption spectra of **2** measured in 2-MeTHF at 297 K using the pump wavelength of (a) 490 and (b) 510 nm, respectively.

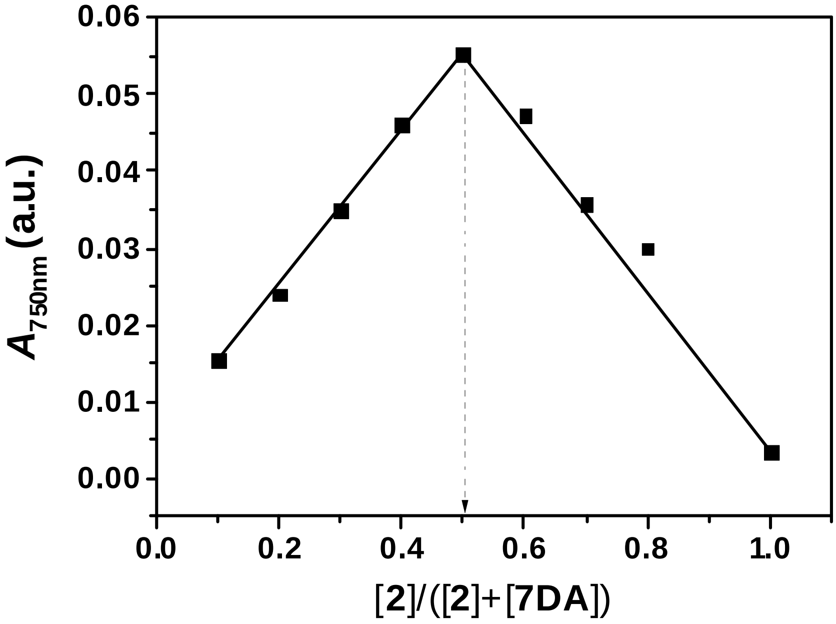
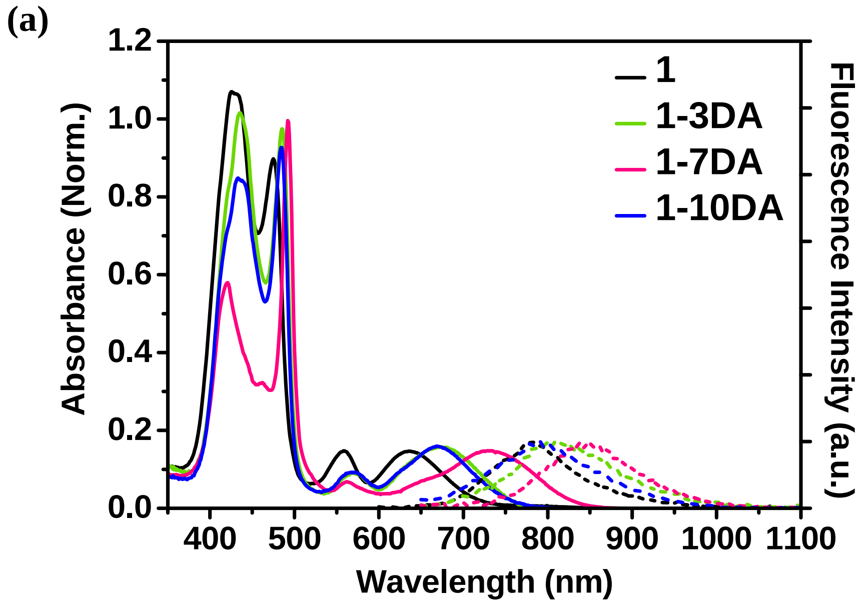


Fig. S6 Job's plot of **2-7DA**. The absorbance at 750 nm versus the molar fraction of **2** ([**2**]/([**2**]+[**7DA**]) is plotted. Initial molar concentration of **2** and **7DA** used was 2.32x10^{-6} M for both.



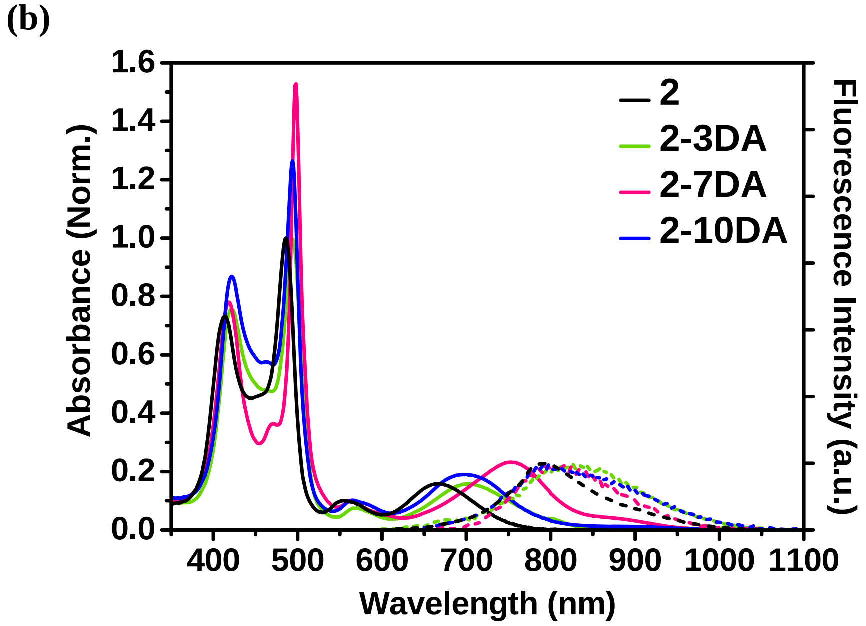


Fig. S7 Steady-state absorption and fluorescence emission spectra of the uncoordinated species (black) and **3DA** (green), **7DA** (magenta), and **10DA** (blue) complexes of (a) **1** and (b) **2**. The excitation wavelength employed for the fluorescence measurement was 442 nm. The molar concentrations employed were 1.5×10^{-6} M for both the hosts and the guests in (a) and 3.0×10^{-6} M for all components in (b). The ligands were added in excess where there was no further change in the absorption spectra after forming 1:1 complexes.

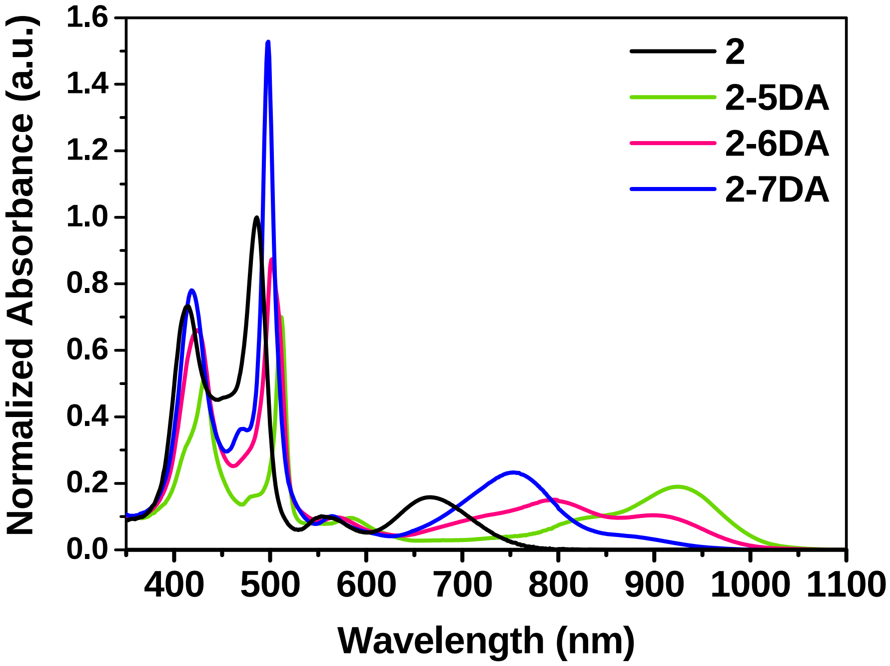


Fig. S8 Steady-state absorption spectra of **2-5DA** (green), **2-6DA** (magenta) and **2-7DA** (blue) along with that of uncoordinated **2** (black) at room temperature. [**2**] = [**5DA**] = [**6DA**] = [**7DA**] = 3.0×10^{-6} M, and the ligands were added in excess where there was no further change in the absorption spectra after forming 1:1 complexes.

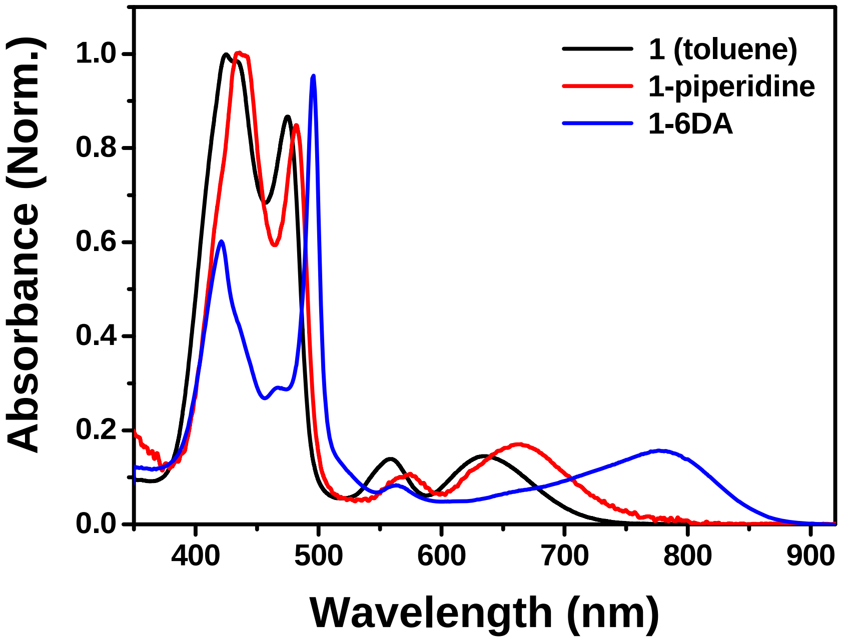


Fig. S9 Steady-state absorption spectra of control complexes of **1** and monodentate amine ligands (piperidine; red) in comparison with uncomplexed **1** (black) and **1-6DA** (blue). The ligands were added in excess where there was no further change in the absorption spectra after forming 1:1 complexes.

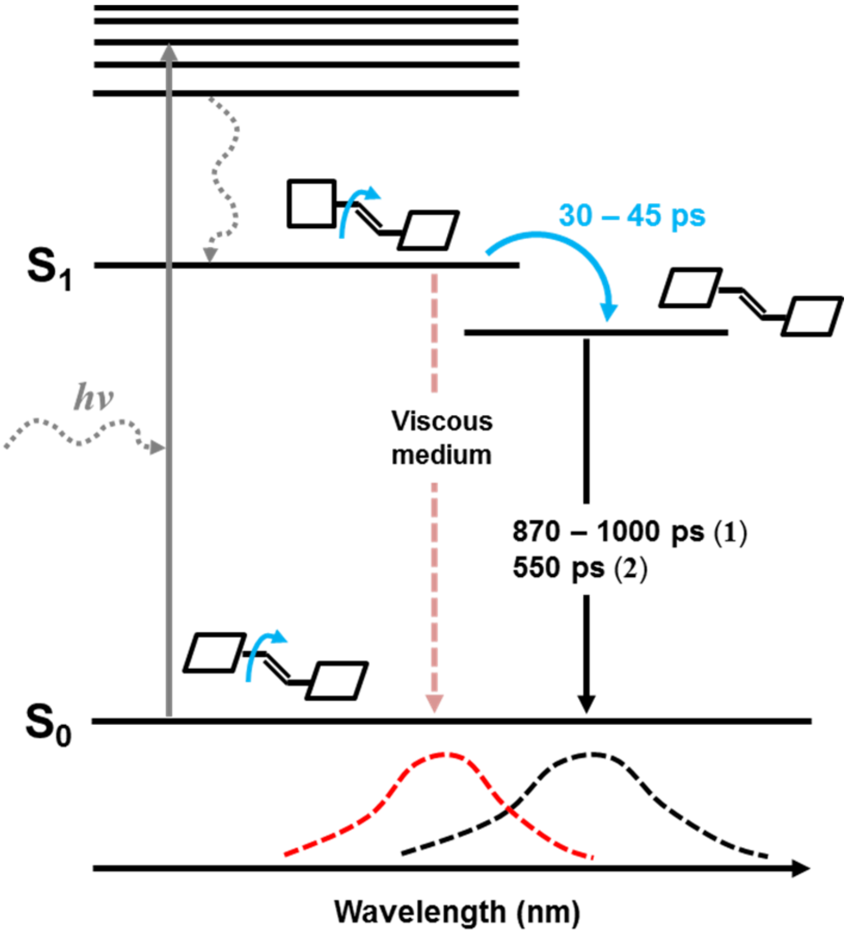


Fig. S10 Schematic illustration of the conformational dynamics described in this article.

3. References

1. S. Tokuji, H. Awane, H. Yorimitsu and A. Osuka, *Chem. Eur. J.,* 2013, **19**, 64.