Electronic Supplementary Information

Comparative Photophysical Properties between BCOD- and Benzo-fused Free-base Triphyrins (2.1.1)

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Experimental Details

Temperature Dependent Experiments. For the temperature-dependent steady-state and time-resolved absorption and emission studies, a temperature-controlled liquid nitrogen cryostat (Oxford Instruments: Optistat DN) was used. The variable temperature femtosecond transient absorption experiments were conducted using a Janis VNF-100 cryostat with a Cryo-con 32B temperature controller. Temperatures were maintained to within ±0.05 K and allowed to equilibrate for 30 minutes before spectroscopic measurements. The samples were degassed with Ar gas in order to exclude any effects from quenching reactions caused by oxygen. The results were controlled by comparison with measurements in a regular cuvette at room temperature, as possible. In our experiment, all spectra were measured in m-THF solvent.

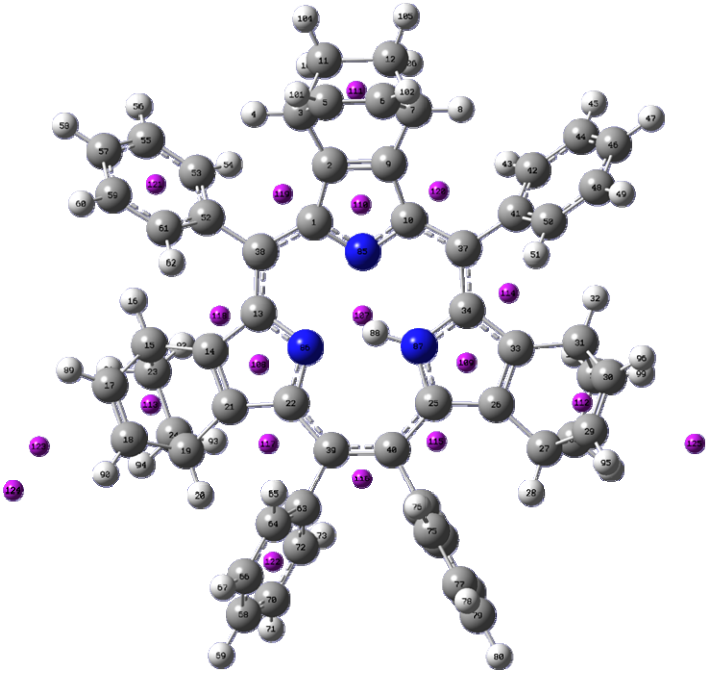
Steady-state Absorption and Emission Measurements. Steady-state absorption spectra were obtained with an UV-VIS-NIR spectrometer (Varian, Cary5000). For the observation of steady-state emission spectra, Steady-state fluorescence spectra were recorded on a fluorescence spectrometer (Sinco, FS-2). In our experiment, all spectra were measured in toluene solvent except for temperature dependent experiment.

Time Correlated Single Photon Counting Measurements. Time-resolved fluorescence lifetime experiments were performed by the time-correlated single-photon-counting (TCSPC) technique. As an excitation light source, we used a Ti:sapphire laser (Mai Tai BB, Spectra-Physics) which provides a repetition rate of 800 kHz with ~ 100 fs pulses generated by a homemade pulse-picker. The output pulse of the laser was frequency-doubled by a 1 mm thickness of a second harmonic crystal (β-barium borate, BBO, CASIX). The fluorescence was collected by a microchannel plate photomultiplier (MCP-PMT, Hamamatsu, R3809U-51) with a thermoelectric cooler (Hamamatsu, C4878) connected to a TCSPC board (Becker&Hickel SPC-130). The overall instrumental response function was about 25 ps (the full width at half maximum (fwhm)). A vertically polarized pump pulse by a Glan-laser polarizer was irradiated to samples, and a sheet polarizer, set at an angle complementary to the magic angle (54.7°), was placed in the fluorescence collection path to obtain polarization-independent fluorescence decays.

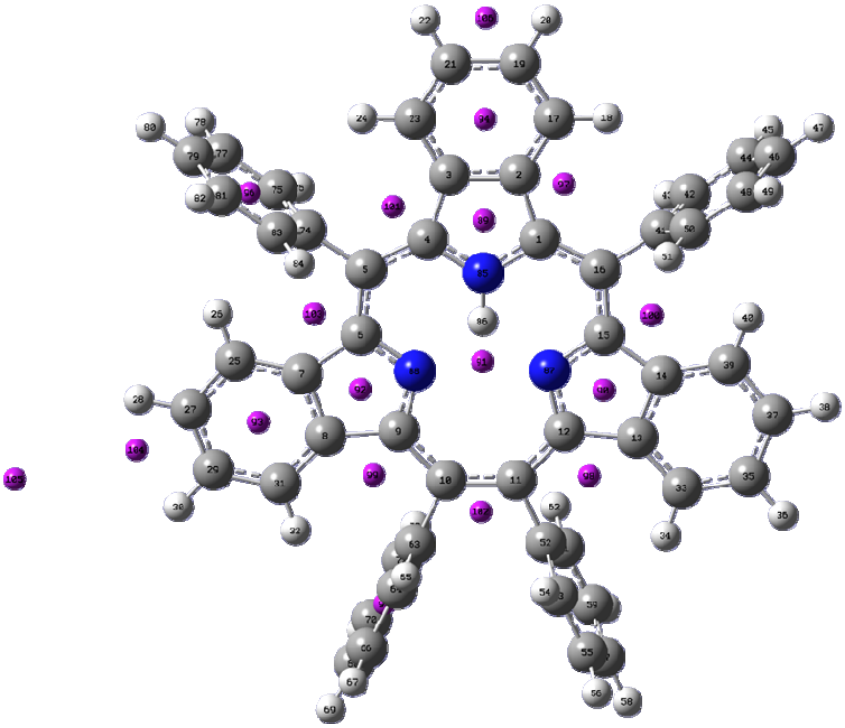
Femtosecond Transient Absorption Measurements. The femtosecond time-resolved transient absorption (TA) spectrometer pumped by a Ti:Sapphire regenerative amplifier system (Quantronix, Integra-C) operating at 1 kHz repetition rate and an optical detection system. The frequency doubled 400 nm pulses had a pulse width of ~ 100 fs and an average power of 1 mW which were used as pump pulses. White light continuum (WLC) probe pulses were generated using a sapphire window (2 mm of thickness) by focusing of small portion of the fundamental 800 nm pulses. The time delay between pump and probe beams was carefully controlled by making the pump beam travel along a variable optical delay (Newport, ILS250).

Intensities of the spectrally dispersed WLC probe pulses are monitored by miniature spectrograph (OceanOptics, USB2000+). To obtain the time-resolved transient absorption difference signal (ΔA) at a specific time, the pump pulses were chopped at 25 Hz and absorption spectra intensities were saved alternately with or without pump pulse. Typically, 6000 pulses excite samples to obtain the TA spectra at a particular delay time. The polarization angle between pump and probe beam was set at the magic angle (54.7°) 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 probe beam path and 2 mm path length of quartz cell were used. 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. In our experiment, all spectra were measured in toluene solvent.

Computational Methods. Quantum mechanical calculation were performed with the Gaussian 03 program suite. All calculations were carried out by the density functional theory (DFT) method with Becke's three-parameter hybrid exchange functionals and the Lee-Yang-Parr correlation functional (B3LYP), employing the 6-31G* basis set. The oscillator strength was calculated by performing time dependent (TD)-DFT calculation.



1 Bq Isotropic = 13.4045
2 Bq Isotropic = 8.9125
3 Bq Isotropic = 0.851
4 Bq Isotropic = 0.5857
5 Bq Isotropic = -0.6666
6 Bq Isotropic = -0.5727
7 Bq Isotropic = 4.104
8 Bq Isotropic = 3.9959
9 Bq Isotropic = -0.7876
10 Bq Isotropic = 11.6373
11 Bq Isotropic = -1.1433
12 Bq Isotropic = 3.1254
13 Bq Isotropic = 2.894
14 Bq Isotropic = 7.8795



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3 Bq Isotropic = -1.8924
4 Bq Isotropic = 5.6521
5 Bq Isotropic = 0.7348
6 Bq Isotropic = -3.1016
7 Bq Isotropic = -2.9281
8 Bq Isotropic = 1.9988
9 Bq Isotropic = -2.9274
10 Bq Isotropic = -3.1025
11 Bq Isotropic = -2.224
12 Bq Isotropic = 10.2146
13 Bq Isotropic = 8.955
14 Bq Isotropic = 7.4689

Figure S1. NICS (0) calculation data (top = **1**, bottom = **2**).

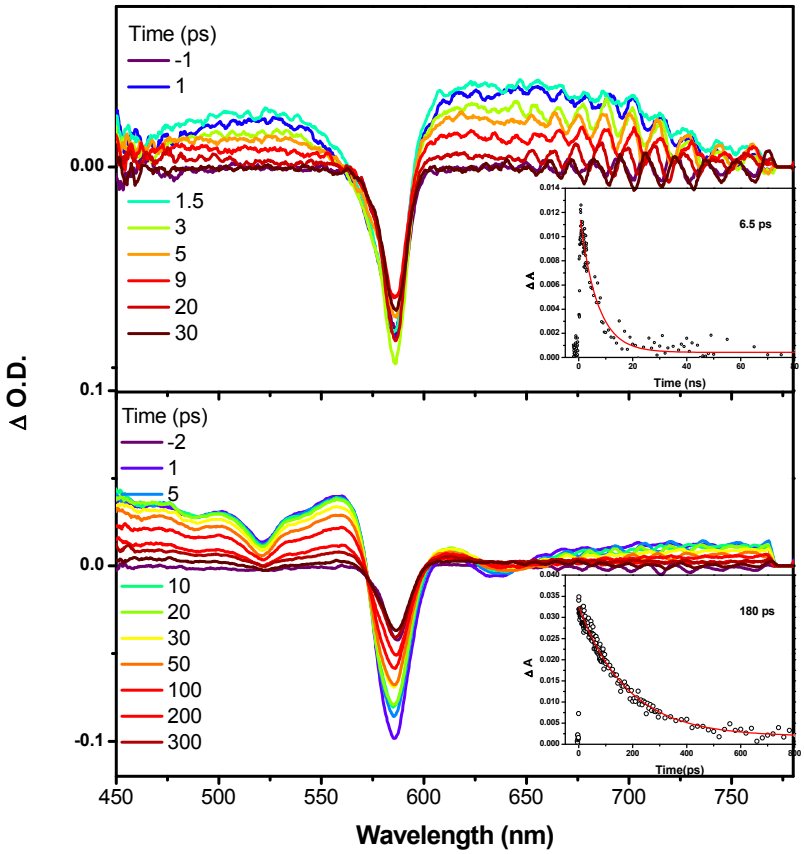

Figure S2. Transient absorption spectra (top: **1**, bottom: **2**, lifetime of **1**: 6.5 ps, lifetime of **2:** 180ps). Inset shows fluorescence decay profiles of the two triphyrins **1** and **2** monitored at 480 and 640 nm, respectively. All spectra were measured in toluene.

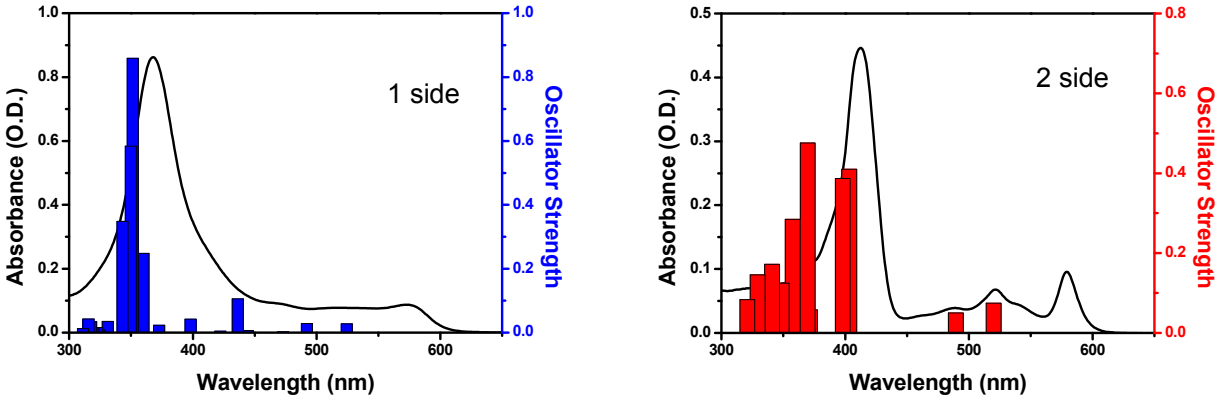

Figure S3. TD-DFT calculation data (left = **1**, right = **2**).

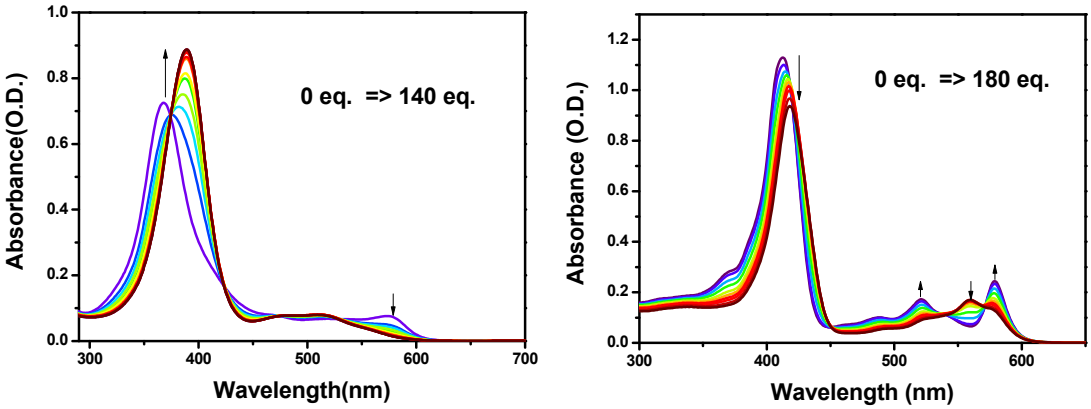

Figure S4. Absorption spectra of protonated forms of the two triphyrins **1** and **2** (left = **1**, right = **2**). All spectra were measured in toluene solvent.

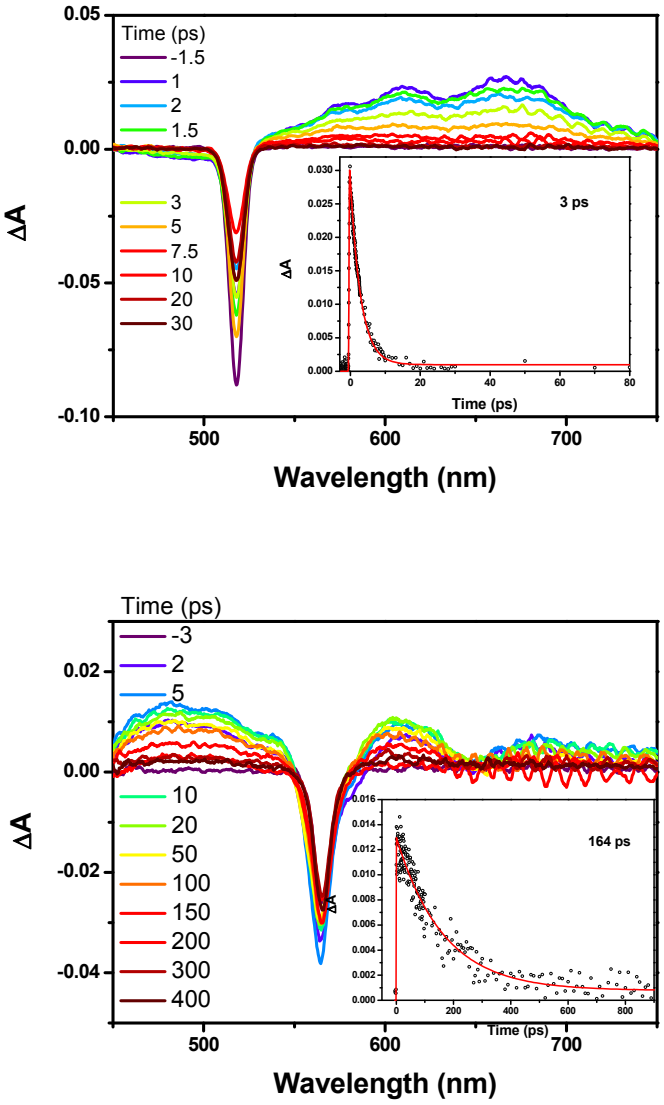

Figure S5. Transient absorption spectra of protonated forms of the two triphyrins **1** and **2** (top: **1**, bottom: **2**, lifetime of **1**: 3 ps, lifetime of **2**: 164 ps). Inset shows fluorescence decay profiles of **1** and **2** monitored at 486 and 659 nm, respectively. All spectra were measured in toluene.