

Supporting Information for

**Characterization of Ultrafast Intramolecular Charge Transfer  
Dynamics in Pyrenyl Derivatives: Systematic Change on Number  
of Peripheral *N,N*-dimethylaniline Substituents**

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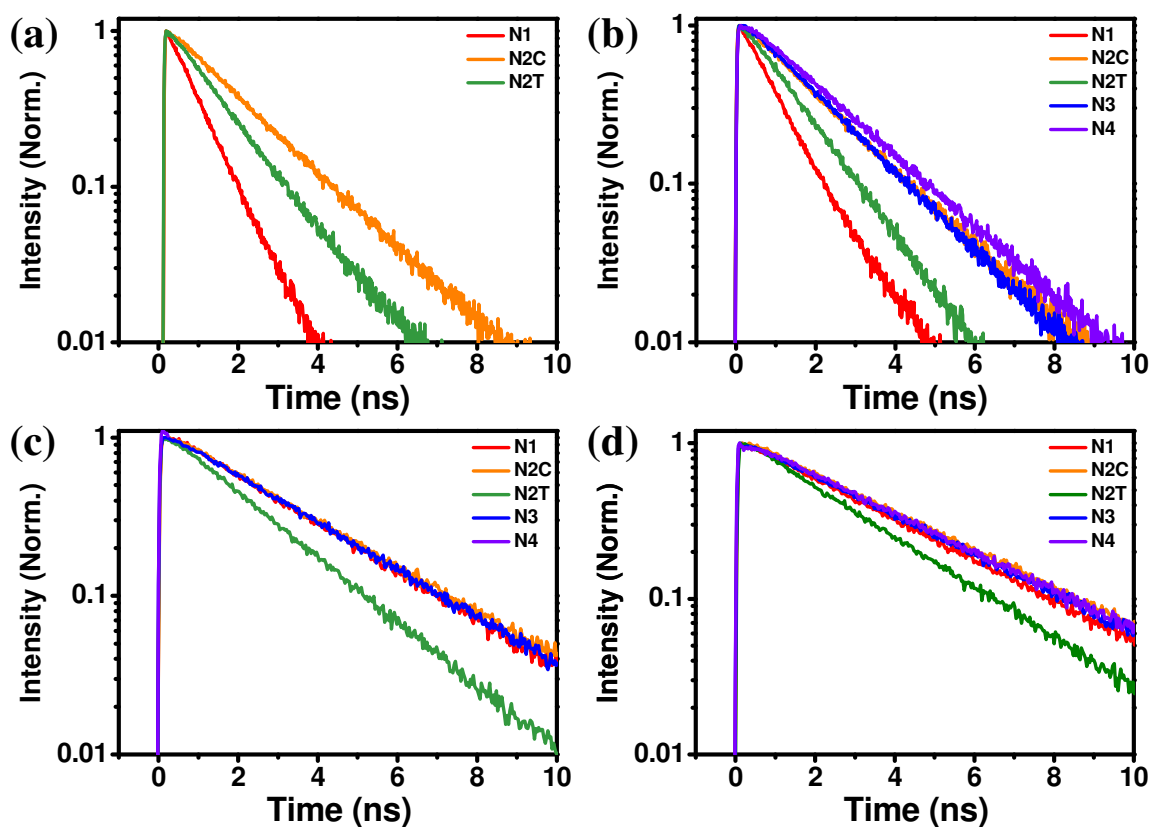
## Synthesis

We synthesized alkynylpyrene derivatives **N1**, **N2C**, **N2T**, **N3**, and **N4** that consist of pyrene as an acceptor moiety, *N,N*-dimethylaniline(DMA) as a peripheral donor moiety, and an ethynyl group as a spacer (Scheme 1).<sup>1,2</sup>

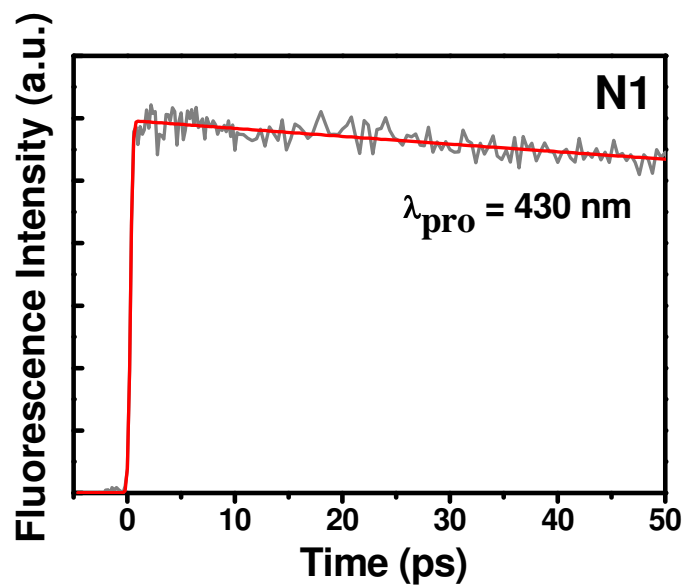
**Table S1.** Calculated Ground State and Excited State Dipole Moments Derived from the Slopes ( $m_f$ ) of the Lippert-Matage function.

	Stokes shift (cm <sup>-1</sup> )						$\mu_g^a$ (D)	$a^b$ (Å)	$m_f^c$ (cm <sup>-1</sup> )	$\mu_e$ (D)
	Toluene	Chloroform	EA	THF	MC	BCN				
N1	2532	3894	4998	4998	4912	5557	4.14	4.27	4.14	14.26
N2C	1581	2272	3264	3246	3246	4072	6.42	4.81	6.42	16.89
N2T	1439	2101	3116	3102	3102	3944	0.01	4.81	0.01	10.50
N3	1162	1606	2343	2297	2322	3297	3.83	5.26	3.83	14.31
N4	1036	1230	1265	1203	1496	1915	0.00	5.54	0.00	6.23

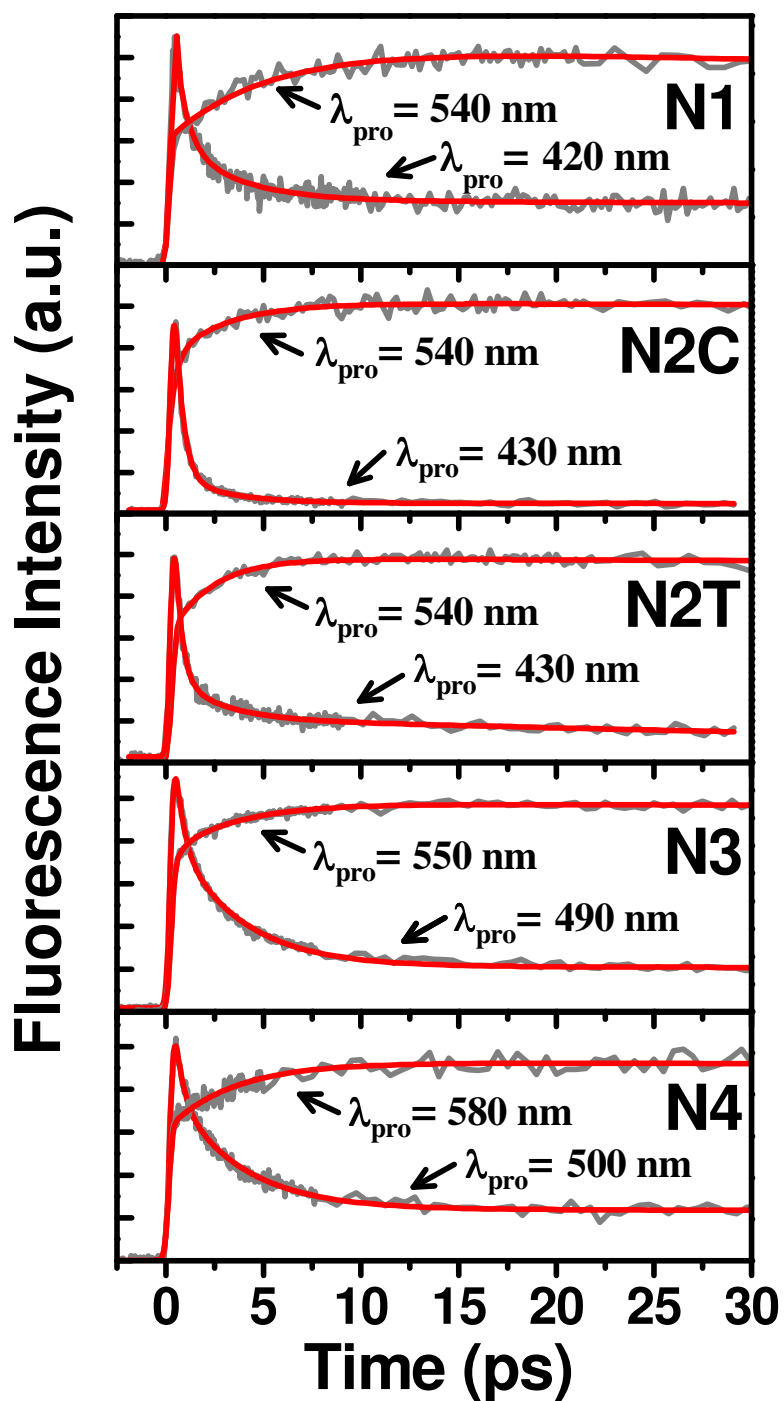
<sup>a</sup> Calculated by DFT method with B3LYP /6-31G\*. <sup>b</sup> Onsager radius estimated from the Van der Waals increment method<sup>3</sup>. <sup>c</sup> the slopes calculated from the plot  $\nu_a - \nu_f$  versus  $\Delta f$ .



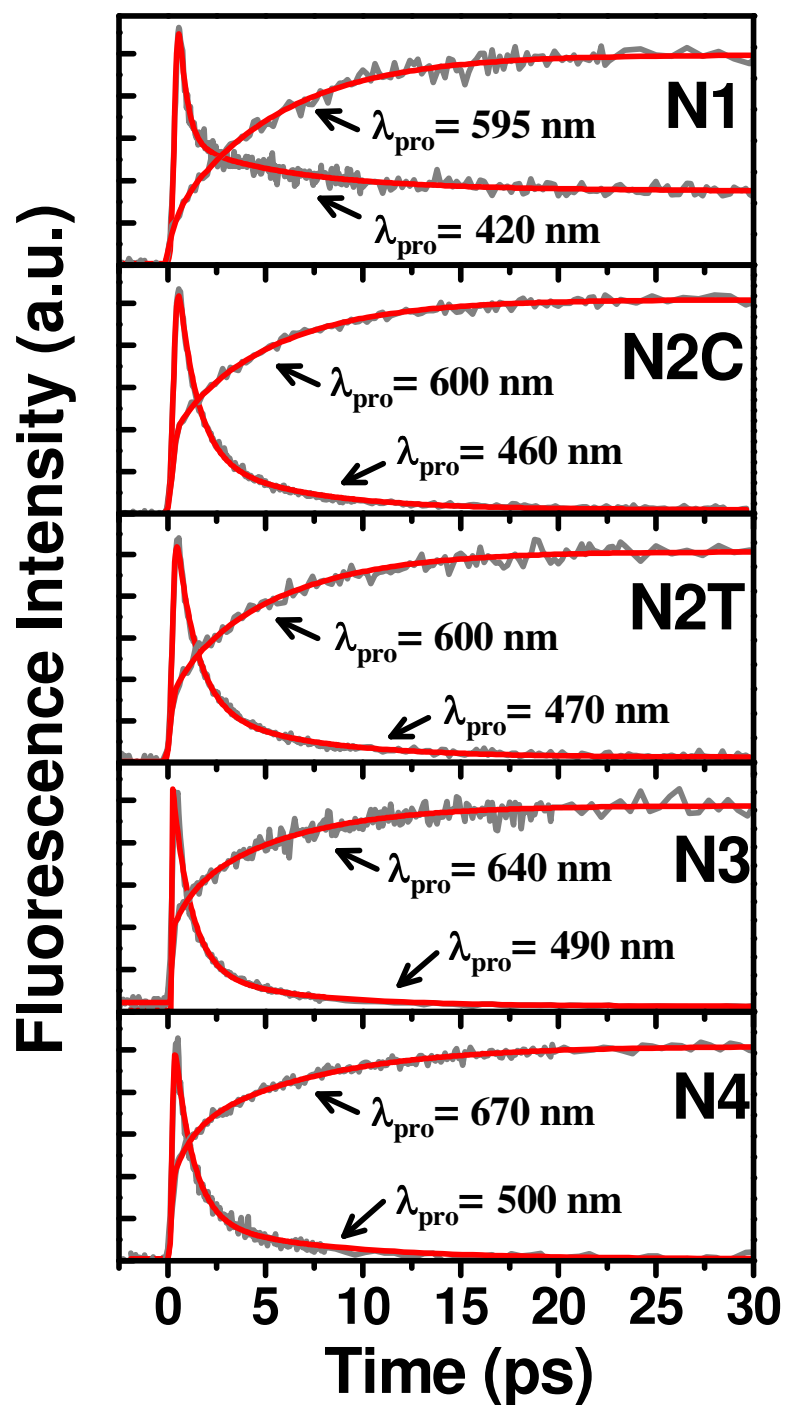
**Figure S1.** Fluorescence lifetime decay profile of N1 (red line), N2C (orange line), N2T (green line), N3 (blue line) and N4 (purple line) in (a) CHX, (b) toluene, (c) THF and (d) BCN were measured by TCSPC using the excitation wavelength of 400 nm. All the fluorescence decay profiles were recorded at their fluorescence band maximum respectively.



**Figure S2.** The fluorescence up-conversion decay profile of N1 in CHX does not exhibit fast decay or rise components and fitted with time constant of 800 ps obtained from TCSPC measurement. This feature indicate that the fluorescence up-conversion decay profile in polar solvent reflect the CT dynamics.



**Figure S3.** Fluorescence decay profiles of N1, N2C, N2T, N3 and N4 in toluene obtained by femtosecond fluorescence up-conversion technique. Each decay profiles were obtained by photoexcitation at 400 nm.



**Figure S4.** Fluorescence decay profiles of N1, N2C, N2T, N3 and N4 in BCN obtained by femtosecond fluorescence up-conversion technique. Each decay profiles were obtained by photoexcitation at 400 nm.

## Experimental Methods

**Steady-state Absorption and Fluorescence Spectra.** Steady-state absorption spectra were acquired using an UV-VIS-NIR spectrometer (Varian, Cary5000). Steady-state fluorescence spectra were recorded on a fluorescence spectrometer (Sinco, FS-2). The fluorescence quantum yield was obtained in comparison to the fluorescence quantum yield of ~0.95 of Rhodamin 6 G in ethanol at ambient condition.

**Picosecond Time-Resolved Fluorescence Decay.** 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 ( $\beta$ -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 ( $54.7^\circ$ ), was placed in the fluorescence collection path to obtain polarization-independent fluorescence decays.

**Femtosecond Time-resolved Fluorescence Decay.** A femtosecond fluorescence up-conversion apparatus was used for the time-resolved spontaneous fluorescence. The beam sources for B and Q state fluorescence were a mode-locked Ti:sapphire laser also used in TCSPC system. The second harmonic of the fundamental generated by a 200- $\mu\text{m}$  thick BBO crystal served as pump pulse. Residual fundamental pulse was used as a gate pulse. The pump beam was focused onto a 500- $\mu\text{m}$  thick quartz cuvette containing sample solution using a 5-cm focal length plano-convex lens with a magic angle ( $54.7^\circ$ ) in order to prevent polarization-dependent signals. The cuvette was mounted on a motor-driven stage and

moved constantly back and forth to minimize photo-degradation. Collection of the fluorescence and focusing into a 1 mm-thick BBO crystal for frequency conversion was achieved by a reflecting microscope objective lens (Coherent). The FWHM of the cross-correlation function between the scattered pump pulse and the gate pulse is measured to be ~310 fs. The average excitation power was kept at a level below 2 mW in order to minimize thermal lens effect. In this excitation intensity regime the fluorescence dynamics was independent of the excitation intensity for all samples.

## References

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