

Supporting Information

Ligand π -Conjugation Dictated Intersystem Crossing in Phenyleneethynylene Gold (I) Complexes

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Experimental details: The instrumental set-ups for femtosecond transient absorption (fs-TA), fs time-resolved fluorescence (fs-TRF) and nanosecond time-resolved emission (ns-TRE) and the related spectral calibrations have been described previously.^{1,2} Briefly, all these measurements were performed based on a commercial Ti:Sapphire regenerative amplifier laser system (800 nm, 40 fs, 1 kHz, and 3.5 mJ/pulse). A 280 nm excitation wavelength was used for all the measurement. The 280 nm pump pulse was produced from the second harmonic of the sum frequency generation between an OPA output and the 800 nm fundamental laser pulse. In the fs-TA, the samples were probed by a white light continuum pulse created from a rotating CaF₂ plate pumped by the 800 nm laser. The fs-TRF was measured by employing the Kerr-gate technique.³ A Kerr device comprising a 1 mm thick Kerr medium (benzene contained in a quartz cell) equipped within a crossed polarizer pair was driven by the 800 nm laser pulse (called gating pulse or probe pulse) to function as an ultrafast optical shutter to sample transient fluorescence spectra at various selected pump/probe delays. For both fs-TA and fs-TRF, the temporal delay of the probe to pump pulse was controlled by an optical delay line. The fs-TA or fs-TRF signals were collected by a monochromator and detected with a liquid nitrogen cooled CCD detector. The instrument response function (IRF) of the fs-TA and fs-TRF is wavelength-dependent. As detection wavelength varies from 600 to 280 nm, the IRF varies from ~0.5 to ~2 ps for TRF and ~100 to ~300 fs for TA. For the ns-TRE measurement, an intensified CCD (ICCD) detector, which was synchronized to the fs laser system, was used to detect transient emission spectra with the controlled pump/probe time delay covering from ~2 ns and afterwards. To eliminate the effect of rotational diffusion, the polarization direction of the pump laser was set at the magic angle in relative to that of the probe for all the measurements. The measurements were done at room temperature and atmospheric pressure with the samples (concentration of ~1 mM) of ~15 ml flowed in a cell with 0.5 mm path length. In the ns-TRF, the sample solutions were purged with nitrogen gas to diminish the oxygen quenching effect. The samples were monitored by UV-vis absorption and revealed no degradation after the time-resolved measurement.

The compounds studied (**1a-3a** and **2b-3b**) in this work were synthesized and characterized according to the methods reported in our earlier work.^{2,4}

Fig. S1 fs-transient absorption spectra (a) and kinetic time profiles at the indicated wavelengths (b) of **1a** in CH₃CN recorded at the indicated decay times after excitation at 280 nm.

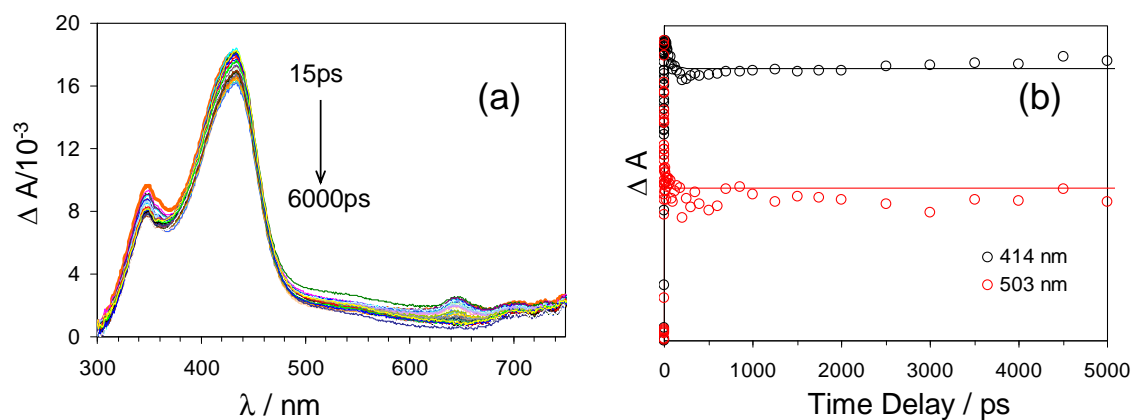


Fig. S2 steady state UV-vis absorption (left) and emission (right) spectra of **1b**, **2b** and **3b** in CH₃CN.

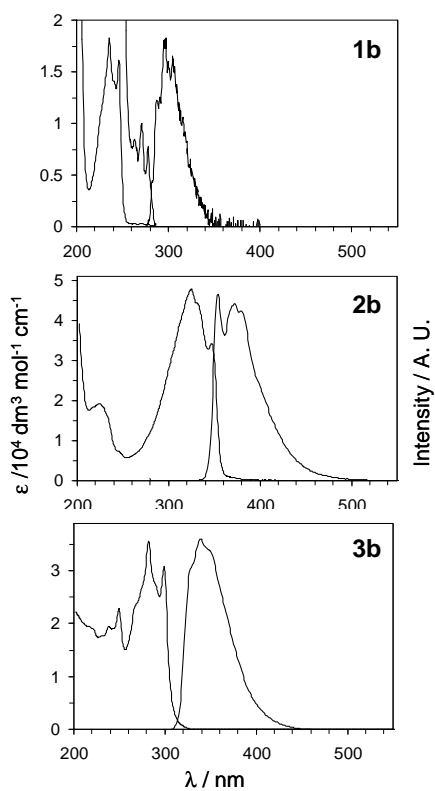


Fig. S3 experimental (circle) and fitted (solid line) decay trace of **1a** in deoxygenated CH₃CN.

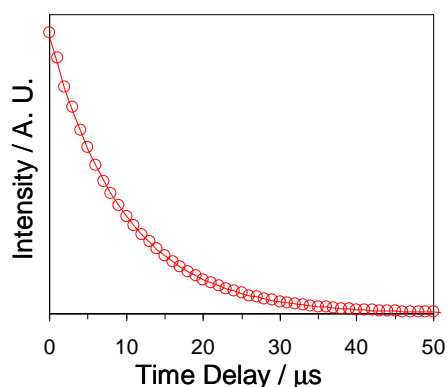
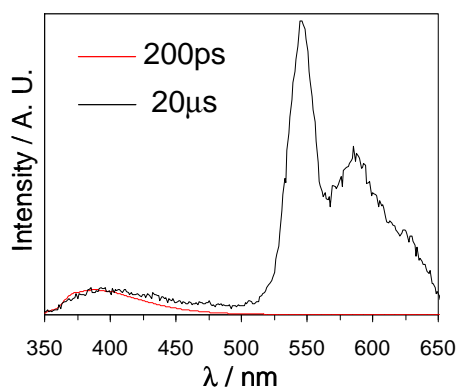


Fig. S4 comparison of spectrum obtained at the indicated delay times from fs-time resolved fluorescence (red) and ns time-resolved emission (black) measurements of **2a** in deoxygenated CH₃CN after 280nm excitation.



References:

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