

## Supporting Information

### Elucidation of Control Mechanisms Discovered During Adaptive Manipulation of $[\text{Ru}(\text{dpb})_3](\text{PF}_6)_2$ Emission in the Solution Phase

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**Expanded Laser Methods:** The laser set up has been described in detail elsewhere<sup>1</sup> and is similar to one used by the Gerber group.<sup>2</sup> Briefly, a broad-band laser pulse train ( $\sim 800$  nm  $\pm$  17 nm;  $\sim 50$  fs temporal FWHM; 1 KHz;  $\sim 900$   $\mu\text{J}/\text{pulse}$ ) is derived from a Ti:Sapphire source consisting of a commercial multi-pass amplifier (Quantronix; Odin) seeded by a commercial Ti:Sapphire oscillator (K&M Labs). The oscillator is pumped by the second harmonic of a continuous wave Nd:YVO<sub>4</sub> laser (Coherent; Verdi) and the amplifier is pumped by the second harmonic of a pulsed Nd:YLF laser (Quantronix; Darwin). The amplified pulse train ( $\sim 20\%$  of total power) is coupled into a home-built pulse shaper constructed in the geometry of a 4f zero-dispersion compressor.<sup>3-5</sup> A pixilated dual-layer computer-controlled spatial light modulator (SLM) (CRI Inc; SLM-640) is placed at the Fourier plane of the pulse shaper. The SLM has 640 individually addressable pixels but only  $\sim 200$  are needed to span the laser spectrum. The index of refraction at each layer of each pixel is independently varied by application of a drive voltage ranging between 0 – 10 volts with 12-bit resolution. The applied voltage is converted to applied phase by means of a home-built calibration procedure and then the phase is modulated modulo  $2\pi$  ( $0-2\pi$ ) over a drive voltage range spanning  $\sim 0$  to  $\sim 2.3$  V. For phase only shaping, the phase retardation is fixed to the same value at each layer of each pixel. For amplitude-only shaping, we independently vary the phase retardation at each layer of each pixel of the SLM. Because a polarizer is placed at the output of the SLM, arbitrary frequency-dependent pulse attenuation is possible.<sup>6</sup> Simultaneous phase and amplitude shaping is also possible with this configuration but this technique was not used during the experiments described herein. The number of pixels used in a given experiment is chosen by inspection to include greater than 95% of the spectral intensity as detected on an Ocean Optics SD2000 spectrometer. For the ratio experiment this was

192 pixels and for the ratio spectrum this was 204 pixels. The background phase acquired from propagation through the optics and possible misalignment of the compressor in the amplifier is corrected for by measuring the phase necessary to maximize the second harmonic of the laser pulse in an independent optimization experiment run prior to the optimization experiments discussed.<sup>2, 7-10</sup>

The output of the pulse shaper is split into two pulse trains. The first ( $\sim 8$  mW) is loosely focused on a 298 K sample of  $[\text{Ru}(\text{dpb})_3](\text{PF}_6)_2$ , (where  $\text{dpb} = 4,4'$ -diphenyl-2,2'-bipyridine) in acetonitrile ( $\sim 9 \times 10^{-5}$  M; 1 cm path length). As shown in **Figure 1** of the manuscript, the molecule absorbs negligibly at wavelengths contained in the pulse train. However, electronic excitation can occur if the molecule absorbs two or more photons from the shaped field. The relative multi-photon excitation efficiency is monitored by collecting a spontaneous emission signal at  $640 \pm 5$  nm from the thermalized triplet  $^3[\text{MLCT}]$  (metal-to-ligand charge transfer) state.<sup>11, 12</sup> We use a negatively biased PMT (Hamamatsu; H9305-02) with  $\sim 1.4$  ns resolution. Box-car averaging (Stanford Research Systems; SR8 10 DSP) between  $\sim 0.1$   $\mu\text{s}$  and  $\sim 1.5$   $\mu\text{s}$  after shaped excitation insures that no scattered laser light or white light generation contaminates the  $^3[\text{MLCT}]$  signal. It should be noted, however, that we attenuate the laser intensity well below the threshold for white light generation. The second pulse train ( $\sim 8$  mW) is loosely focused onto a GaP-Photodiode (FGAP71; Thorlabs) with a rise time of 1 ns at a bias of 5V. Because the spectral response of the GaP-Photodiode (150 nm - 550 nm) is negligible at the wavelengths contained in the pulse train, the measured signal is proportional to the integrated second harmonic (SH) spectrum (a.k.a., two-photon power spectrum) of a laser pulse.<sup>13</sup> In order to measure the SH-spectrum of our laser pulses we insert an additional pickoff into the beam path to produce a third pulse train. The optional third pulse train ( $\sim 5$  mW) is transmitted through a 100  $\mu\text{m}$  beta-barium borate (BBO) crystal (Type I, 30°) to generate the second harmonic of the fundamental. The output is passed through a glass prism to spatially separate the SH signal from the unconverted fundamental. The SH-spectrum is detected by scattering the second harmonic into an Ocean Optics SD2000 spectrometer. All signals reported in the manuscript originating from pulse trains one and two are detected without the additional pickoff inserted in the beam path.

Optimization experiments in our laboratory utilize an iterative learning loop that is comprised of (1) a computer controlled laser pulse shaper, (2) measurement of a molecular response for feedback, and (3) a computer-driven evolutionary algorithm.<sup>14, 15</sup> The heuristic search methodology is based on metaphors of evolutionary biology and is capable of accommodating the massive multidimensional parameter space ( $> 10^{400}$ ). The ratio experiment was initialized by randomly coding 60 numerical arrays (termed individuals) of 192 phase values to be applied to the pixels of the SLM. These individuals are thought of as having a genetic code made up of the array of applied phase values. For each generation, the 60 pulses were ranked in terms of their fitness (emission/SHG). To create a new generation, the algorithm rendered a new population of 60 individuals by administering evolutionary operators which crossed-over, mutated, and cloned the genetic material of a selection of the fittest individuals in the previous generation. For each crossover operation, two individuals were chosen by tournament selection and yielded two children; 30 new individuals were produced in this manner. For each mutation operation, an individual was randomly selected from among the ten fittest; 20 new individuals were produced in this manner. The 10 fittest individuals were also cloned to yield 10 new individuals. The population size of 60 individuals was held constant throughout the experiment. The algorithm ran for 300 generations (18,000 pulses) and improved the ratio by a factor of  $\sim 1.4$ . After the experiment had finished, the optional pickoff was inserted and the SH spectra for the best pulse of generations 0, 50, 100, 150, 200, 250, and 299 were measured.

**Expanded Theory:** Gerber's group has described how perturbation theory of two-photon light-matter interactions offers a *possible* explanation for control of the ratio emission/SHG in the system described in the manuscript.<sup>2</sup> According to the theory, since emission reports the extent to which excited-state population is created by the input field, the ratio of emission/SHG can be modulated if spectral properties of the shaped field take advantage of molecule-specific features in the two-photon absorption spectrum which are absent in the SHG response (assumed to be constant across the laser spectrum). The theory builds upon work by Noordham's group and Silberberg's group.<sup>16-18</sup>

It has been shown that, absent any real intermediate, an electric field  $E(t)$  (corresponding to a weak femtosecond pulse) can induce two-photon transitions from an initial state  $|i\rangle$  to a final state  $|f\rangle$  via some imaginary state  $|n\rangle$ . If one assumes the intermediate levels are very far from resonance, then the final-state population  $p_{TPA}(\omega)$  is proportional to the product of two terms:

$$p_{TPA}(\omega) \propto g_{TPA}^{(2)}(\omega) S^{(2)}(\omega) \quad (1)$$

In this expression,  $g_{TPA}^{(2)}(\omega)$  is a molecule-specific term detailing the probability of two-photon excitation (a.k.a., two-photon absorption) as a function of frequency  $\omega$ . In essence, this determines the frequency range where the *molecule* is most susceptible to two-photon excitations:

$$g_{TPA}^{(2)}(\omega) \propto \left| \sum_n \frac{\mu_{fn} \mu_{ng}}{\omega_{ng} - \omega/2} \right|^2 \quad (2)$$

In this expression,  $\mu_{fn}$  and  $\mu_{ng}$  are the dipole matrix elements between the final and intermediate states and the intermediate and initial state, respectively. The frequency  $\omega_{ng}$  is proportional to the energy differences between the final and intermediate states and the intermediate and initial states according the standard formula  $\hbar\omega_{ij} = E_i - E_j$ . On the other hand,  $S^{(2)}(\omega)$  is entirely field-dependent and describes the two-photon power spectrum. In essence, this determines the frequency range where the *laser* is most apt to induce two-photon excitations:

$$S^{(2)}(\omega) \propto \left| \int_{-\infty}^{\infty} d\omega' E(\omega) E(\omega - \omega') \right|^2 \quad (3)$$

In this expression,  $E(\omega) = |E(\omega)|\exp[i\Phi(\omega)]$  is the Fourier transform of  $E(t)$ . In the experiment, the two-photon power spectrum is modulated by varying  $\Phi(\omega)$ , which is the frequency-dependent phase applied by pulse shaper.

The theory of nonresonant SHG in a thin nonlinear optics crystal is also well known.<sup>19, 20</sup> In brief, in the limit of no pump depletion and sufficient acceptance bandwidth in the crystal, the intensity of the second harmonic signal is proportional to the two-photon power spectrum:

$$I_{SHG}(\omega) \propto S^{(2)}(\omega) \quad (4)$$

Therefore, the fitness  $f$  (emission/SHG) of any laser pulse is proportional to the ratio of Eq. 1 integrated over all  $\omega$  contained in the shaped laser field and Eq. 4 integrated over all  $\omega$  contained in the shaped laser field:

$$f \propto \frac{\int p_{TPA}(\omega)d\omega}{\int I_{SHG}(\omega')d\omega'} \propto \frac{\int g_{TPA}^{(2)}(\omega)S^{(2)}(\omega)d\omega}{\int S^{(2)}(\omega')d\omega'} \quad (5)$$

It can be seen that the pulse fitness is entirely determined by the two-photon excitation spectrum  $g_{TPA}^{(2)}(\omega)$  and the SH spectrum  $S^{(2)}(\omega)$ . Note that this equation is given as **Eq. 1** in the manuscript. Because the two-photon excitation spectrum is an intrinsic (and unchangeable in the perturbation theory) property of the molecular system, the observed fitness can only be manipulated by changing the SH spectrum, which, as shown above, is achieved by varying the spectral phase (i.e., pulse shaping). Furthermore, note that if the width of the pulse is narrow around a central frequency  $\omega_0$ , the fitness may be approximated:

$$f \propto \frac{g_{TPA}^{(2)}(\omega_0)S^{(2)}(\omega_0)}{S^{(2)}(\omega_0)} \propto g_{TPA}^{(2)}(\omega_0) \quad (6)$$

This equation (given as **Eq. 2** in the manuscript) is the basis for the measurement of a ratio spectrum as described in the manuscript. In essence, when a narrow band pulse is employed, the ratio (fitness) is a proportional to the two-photon excitation spectrum at the central frequency of the pulse.

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