## Electronic Supplementary Information for

# Coherent vibration and ultrafast dynamics upon bond

## formation in excited dimers of Au(I) complex

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#### **1. Experimental Procedures**

#### **1.1.** Sample preparation

 $K[Au(CN)_2]$  was obtained from Inuisho Precious Metals Co. (99.5 % purity), and it was used after recrystallization several times in water. We also used the sample obtained from Aldrich Co. (99.98 % purity) after recrystallization, and confirmed that both samples give essentially the same absorption and time-resolved emission spectra. We recorded steady-state absorption spectra of the sample solution before and after the time-resolved measurements, and did not recognize any noticeable changes, indicating that photo-degradation of the sample during the measurements is negligible.

#### 1.2. Femtosecond time-resolved absorption spectra

The experimental setup for femtosecond time-resolved absorption measurements was described elsewhere.<sup>1</sup> Briefly, the output from a Ti:sapphire regenerative amplifier system (Legend Elite, Coherent; 800 nm, 80 fs, 1 mJ, 1 kHz) was converted to a near-infrared pulse (1660 nm) by an optical parametric amplifier (TOPAS, Light Conversion), and it was mixed with the 800-nm pulse to generate a sum-frequency pulse at 540 nm. The 540-nm pulse was frequency-doubled to generate an ultraviolet pulse at 270 nm. The 270-nm pulse was used as the pump pulse for photoexcitation of A small fraction of the 800-nm pulse was focused into a CaF<sub>2</sub> plate to the sample. generate a white-light pulse that covers a spectral region of 350 - 750 nm, and it was used as the probe and reference pulses. The pump polarization was set at the magic angle with respect to the probe polarization. The sample solution was circulated through a fused-silica flow cell with a 0.5-mm path length. The probe and reference spectra of every five laser shots were measured with a spectrograph (500 is/sm, Chromex) and a charge-coupled device (CCD) (TEA/CCD-1024-EM/1 UV, Princeton

Instruments) that was read out at a 100-Hz repetition rate. The effect of the chirp of the white-light probe on the time-resolved spectra was corrected based on the optical Kerr effect (OKE) data of water, which was measured with exactly the same experimental configuration.<sup>2</sup> The full width at half maximum (fwhm) of the instrumental response function (IRF) of the system recorded in the OKE measurement was ~ 200 fs.

#### 1.3. Measurements of time-resolved emission spectra and emission lifetimes

Picosecond time-resolved emission data were measured using a lab-made timecorrelated single photon counting (TCSPC) system. The third harmonics (269nm) of the fundamental of a mode-locked Ti:sapphire laser (Tsunami, Spectra Physics, 808 nm, 1W, 80 MHz repetition rate) was generated using BBO crystals (1mm thickness) and separated with a CaF<sub>2</sub> equilateral dispersive prism. The 269-nm light was used for photoexcitation of the sample. The emission from the sample was detected with a monochromator (Jobin Yvon H10) equipped with a microchannel plate photomultiplier (MCP-PM, Hamamatsu R3809U-51) that was cooled at -30 °C. Signals from the MCP-PM (start pulse) and the photodiode (stop pulse) were amplified with preamplifiers (EG&G Ortec VT120B and Hamamatsu C5594, respectively) and then discriminated with ps-timing discriminators (EG&G Ortec 9307). Those output pulses were fed into a time-to-amplitude converter (TAC, EG&G Ortec 567). The output of the TAC was digitized using an analog-to-digital converter (10 MHz, 12bit) and accumulated on a computer. The fwhm of IRF in our system is typically 40 ps. The TCSPC data were recorded at every 5 nm in the range of 300-400 nm, and they were used to reconstruct time-resolved emission spectra at each delay.

Emission lifetimes in the nanosecond time region were measured by photoexciting the sample solution with the fourth harmonic of a Q-switched Nd<sup>3+</sup>:YAG laser (266nm,

10Hz, Surelight, Contiuum). The emission was spectrally resolved by a grating monochromator (H20, Jobin Yvon), and detected by a photo-multiplier (R5600u03, Hamamatsu). The transient signal from the photo-multiplier was accumulated for 160 laser shots on a digitizing oscilloscope (TDS 694C, Tektronix) to obtain the temporal profile of the emission intensity. The time resolution of this measurement was ~2 ns.

#### **1.4.** Steady-state absorption and emission spectra

Absorption spectra were recorded using a commercial spectrometer (MPS-2000, Shimadzu). Steady-state emission spectra were recorded using a commercial fluorospectrometer (FP8500, JASCO). The spectral sensitivity was corrected using a standard lamp and Rhodamine B quantum counter.

#### **1.5.** Theoretical calculations

Details of the quantum chemical calculations have been reported elsewhere.<sup>1</sup> The optimized geometries and excitation energies of  $[Au(CN)_2^-]_2$  in the lowest triplet (T<sub>1</sub>) state were calculated with the density functional theory (DFT) and time-dependent DFT methods, respectively, using a GAUSSIAN 09 program.<sup>3</sup>

### 2. Absorption Spectra

Aqueous solutions of  $[Au(CN)_2^{-}]$  include not only the monomer but also the dimer and even larger oligomers due to association in the ground state through the aurophilic interaction.<sup>4</sup> To investigate the spectroscopic properties and dynamics of the dimer, it is crucial to selectively excite the dimer among the coexisting species. In this and subsequent sections, we discuss the optimum condition, particularly the sample concentration and excitation wavelength, for selective excitation of the dimer on the basis of steady-state absorption, emission, and transient emission data.

Figure S1a shows absorption spectra of  $[Au(CN)_2^-]$  aqueous solutions with various concentrations in the range of  $10^{-4} - 10^{-1}$  mol/dm<sup>3</sup>. The absorption spectrum varies and extends to the longer wavelength side with increase in the concentration. This spectral behavior can be also seen by a logarithmic plot of apparent extinction coefficients (i.e., absorption intensity divided by concentration) in Figure S1b. In the concentration range of  $10^{-4} - 10^{-3}$  mol/dm<sup>3</sup>, the apparent extinction coefficient does not change, indicating that only monomer predominantly exists in such dilute solutions. The monomer spectrum shows absorption only in the wavelength region below 245 nm with characteristic peaks at 240, 230, 210, 204, and 196 nm.



**Figure S1.** (a)Absorption spectra of K[Au(CN)<sub>2</sub>] aqueous solution at various concentrations from  $1.0 \times 10^{-4}$  to  $0.10 \text{ mol/dm}^3$  (optical path length: 1.0 mm). (b) Logarithmic plots of apparent extinction coefficients.

For higher concentrations such as 0.01 mol/dm<sup>3</sup>, the red part of the absorption spectrum extends to the 280-nm region with a broad shoulder around 260 nm. The appearance of the 260-nm shoulder is clearly seen in Figure S1b. This change in the spectral feature indicates that oligomers are formed at concentrations as high as 0.01 mol/dm<sup>3</sup>. To quantitatively examine the oligomer formation, we examined the concentration dependence of the absorbance of the sample solution at 266 nm (Figure S2).



**Figure S2.** Concentration dependence of the absorbance of  $K[Au(CN)_2]$  aqueous solutions at 266 nm measured with the path length of d = 1 mm.

When the  $[Au(CN)_2]$  aqueous solution contains only the monomer and the dimer, the total concentration ([Au]) is represented as

$$[Au] = [Au1] + 2[Au2], \qquad (S1)$$

where [Au1] and [Au2] denote the concentrations of the monomer and dimer, respectively. Since the two species are in equilibrium, their concentrations are related

as

$$K = \frac{[Au2]}{[Au1]^2} \tag{S2}$$

From equations S1 and  $S_{K}^{2}[Au^{2}]_{\mu}$  is represented by [Au] as  $[Au2] = \frac{8K}{8K}$ 

Because the monomer does not show any absorption at 266 nm, the absorbance of the

$$[Au(CN)_2] aqueous solution at this wavelength (Abs) is represented as
$$Abs = \varepsilon d[Au2] = \frac{8K}{8K}$$
(S4)$$

using the extinction coefficient of the dimer,  $\varepsilon$ .

(S3)

As shown in Figure S2, the equation S4 well reproduces the recorded absorbance at 266 nm in the concentration range of  $[Au] = 0 - 0.04 \text{ mol/dm}^3$ , which gives  $K = 2.65 \text{ dm}^3/\text{mol}$  and  $\varepsilon = 1200 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{cm}^{-1}$ . (Note that effect of ionic strength is negligibly small in this concentration range.) This good agreement suggests that the monomer and dimer coexist as predominant species in the concentration range below 0.04 mol/dm<sup>3</sup>. This accords well with a report by Patterson and coworkers, who concluded that the absorption at 250 – 300 nm is dominated by the dimer in the concentration range below 0.1 mol/dm<sup>3</sup>.

At concentrations as high as 0.1 mol/dm<sup>3</sup>, the longer-wavelength tail of the absorption spectrum further extends to the red beyond 300 nm with a broad shoulder around 295 nm (black curve, Figure S1). This new tail is attributable to the trimer formed in such a highly concentrated solution, because the dimer does not show any significant absorption at wavelengths above 280 nm. This assignment is consistent with our previous observation that photoexcitation of a  $\sim 0.4$  mol/dm<sup>3</sup> solution at 310 nm exhibits spontaneous emission characteristic of the trimer.

To study the dimer, it is desirable (1) to choose the highest possible concentration within the range in which only the monomer and dimer coexist (i.e.,  $< 0.04 \text{ mol/dm}^3$ ), and (2) to excite the solution at a particular wavelength where only the dimer absorbs. With this criterion, we chose the [Au(CN)<sub>2</sub><sup>-</sup>] aqueous solution with the 0.038 mol/dm<sup>3</sup> concentration and photoexcited the sample solution at ~ 270 nm. Actually, a simple monomer – dimer equilibrium holds at 0.038 mol/dm<sup>3</sup>, as described above, and the 270-nm light is only absorbed by the dimer. Under this carefully chosen optimum condition, the dimer is excited highly selectively, as we quantitatively verify by emission measurements.

#### 3. Steady-state and time-resolved emission data

Figure S3 shows a steady-state emission spectrum of the 0.038 mol/dm<sup>3</sup> aqueous solution measured with excitation at 266 nm. This emission spectrum exhibits three emission bands at 330, 400, and 430 nm. The 400-nm and 430-nm bands accord with the emission data reported by Patterson and coworkers, in which they observed two similar bands in both 0.03 and 0.05 mol/dm<sup>3</sup> solutions with 290-nm excitation. With the help of theoretical calculations, they assigned the 400-nm band to phosphorescence from the triplet  $(T_1)$  state of the trimer having the linear staggered structure, whereas the 430-nm band to that of larger oligomers such as tetramers. In frozen methanol at 77 K, they observed additional band at 330 nm, and attributed it to phosphorescence of the trimer that has a non-optimized structure like a bent or eclipsed structure. However, it is very unlikely that such metastable structures are formed in room-temperature Although the peak wavelength of 330-nm is commonly observed, the 330solutions. nm band we observed at room temperature is more likely assignable to phosphorescence of the dimer, rather than the non-optimized trimer, because the dimer emission is expected to appear in the shorter wavelength side compared to the trimer band at 400 This assignment is fully consistent with our TDDFT calculation, which shows nm. that the phosphorescence peak wavelengths of the dimer, trimer, and tetramer having the linear staggered structure are 330 nm, 400 nm and 445 nm, respectively.<sup>1</sup> The fact that the dimer is almost selectively excited under the present condition also supports this assignment, although the 330-nm band is considerably weaker than the two other bands in Figure S3. Since the steady-state emission intensity reflects the lifetime of the emissive state, it is indispensable to clarify the emission dynamics to rationalize the relative band intensity in steady-state emission.



**Figure S3.** Steady-state emission spectrum of K[Au(CN)<sub>2</sub>] aqueous solution (0.038 mol/dm<sup>3</sup>,  $\lambda_{ex} = 266$  nm).

To investigate the emission dynamics of  $[Au(CN)_2]$ , we measured time-resolved emission signals of the 0.038 mol/dm<sup>3</sup> aqueous solution using the TCSPC system with excitation at 269 nm. We recorded the time-resolved signals at various wavelengths in the 310 - 420 nm region, and reorganized them to obtain time-resolved emission spectra at selected delays. As shown in Figure S4a, the time-resolved spectrum at early delays (< 60 ps) exhibits two emission bands at around 330 nm and 400 nm. This observation is consistent with the corresponding two bands in the steady-state emission spectrum, which we assigned to the phosphorescence of the dimer and trimer, respectively. It was found that the dimer emission at 330 nm decays much faster than the trimer emission at 400 nm, and hence only the 400-nm band remains after 120 ps. As shown in Figure S4b, we fit a single exponential function to the emission decay at 330 nm by taking account of the instrumental response, and determined the lifetime of the dimer emission as 25 ps. On the other hand, the lifetime of the trimer emission at 400 nm was determined as 1.6 ns, as shown in Figure S4c. This phosphorescence lifetime of the trimer is in good agreement with the value (2.0 ns) that we measured for the 0.27 mol/dm<sup>3</sup> solution using a streak-camera system.<sup>1</sup> Note that the spiky feature observed at very early delays is due to the dimer emission that spectrally extends to the 400-nm region.

We also tried the TCSPC measurement at 430 nm and longer wavelengths, where the tetramer emission is observed in the steady-state spectrum. However, the recorded signal showed a large offset due to the pile-up effect, implying that the lifetime of the 430-nm emission is longer than the period of the excitation pulse train (~13 ns) used in the TCSPC measurement. Thus, we examined the emission decay at 440 nm by the nanosecond time-resolved emission system with a 10-Hz repetition-rate excitation at 266 nm. As shown in Figure S4d, the obtained temporal trace is well reproduced by a bi-exponential function. The decay time constant of the faster component is instrument-limited (~2 ns) and is attributable to the lifetime of the trimer emission observed around 400 nm, whereas the slower time constant was determined as 27 ns, corresponding to the lifetime of the tetramer emission.

The present time-resolved emission measurement revealed that the phosphorescence lifetimes of the dimer, trimer, and tetramer are 25 ps, 1.6 ns, and 27 ns, respectively, and that they largely differ from one another. This large difference in the phosphorescence lifetime is a reason why the dimer emission is only weakly observed in the steady-state spectrum despite that the dimer is predominantly excited under the present condition. This issue is further verified quantitatively in the following session.



**Figure S4.** (a) Time-resolved emission spectra of K[Au(CN)<sub>2</sub>] aqueous solution (0.038 mol/dm<sup>3</sup>) and time-resolved emission data recorded at (b) 330 nm and (c) 400 nm by TCSPC. Gray area in (b) shows a response function recorded by the emission of the excitation pulse ( $\lambda_{ex} = 269$  nm). (d) Nanosecond time-resolved emission data at 440 nm ( $\lambda_{ex} = 266$  nm). Red lines are the best fits obtained with single (330 nm) or double exponential (400 and 440 nm) functions that are convoluted with the instrumental response. In the 400-nm and 440-nm decays, the time constants of the first components could not be determined from the fitting because they were shorter than the time-resolution of each apparatus we used.

#### Quantitative analysis of the emission data

Since time-integration of the time-resolved emission signal yields the steady-state emission intensity, the relative band intensity in steady-state emission can be translated to the relative population of the initially photoexcited dimer, trimer, and tetramer by quantitative analysis using the evaluated emission lifetimes. For simplicity, we first assume that all the three species coexist in the ground state and that the photoexcited species undergoes intersystem crossing with the quantum yield of unity on the time scale much shorter than the phosphorescence lifetimes. In this case, the time-resolved phosphorescence intensity observed at frequency  $\nu$  is simply written as a sum of the contributions of the three species:

$$I(v,t) = I_2(v,t) + I_3(v,t) + I_4(v,t),$$
(S5)

$$I_{i}(\nu,t) = a_{i}(\nu)N_{i}(t) = a_{i}(\nu)N_{i}^{0}e^{-\nu_{i}t}$$
(S6)

where  $a_i(v)$ ,  $N_i^0$ , and  $\tau_i$  denote the phosphorescence transition probability at frequency v, initial population of the photoexcited molecule, and phosphorescence lifetime, respectively, for the dimer (i = 2), trimer (i = 3), and tetramer (i = 4). Time integration of the time-resolved emission component gives the steady-state emission spectrum due to each species:  $S_i(v) = \int_0^\infty I_i(v,t)dt = a_i(v)N_i^0\tau_i$ . (S7)

Further integration with respect to frequency provides the band area due to each species  

$$(A_i) \text{ in the steady}_{i} = \int_{0}^{\infty} mission spectrum which can be experimentally evaluated:}$$

$$F_i \equiv \int_{0}^{\infty} a_i(v) dv \qquad (S8)$$

$$(S9)$$

Here, the  $F_i$  value is related to the number of emitted photons per unit time from the phosphorescent state, and hence it is proportional to the radiative rate of the corresponding species ( $k_{ri}$ ). Thus, the ratio of the steady-state band areas due to the dimer, trimer, and tetramer is written as

$$A_{2}:A_{3}:A_{4} = F_{2}N_{2}^{0}\tau_{2}:F_{3}N_{3}^{0}\tau_{3}:F_{4}N_{4}^{0}\tau_{4} = k_{r2}N_{2}^{0}\tau_{2}:k_{r3}N_{3}^{0}\tau_{3}:k_{r4}N_{4}^{0}\tau_{4} \quad .$$
(S10)

Assuming that the radiative rates of the three species are not very different from one another ( $k_{r2} \approx k_{r3} \approx k_{r4}$ ), this ratio is finally approximated as

$$A_2: A_3: A_4 \approx N_2^0 \tau_2: N_3^0 \tau_3: N_4^0 \tau_4 \quad . \tag{S11}$$

As shown in Figure S5, we fit a sum of three Gaussian functions to the steady-state emission spectrum (represented in the frequency space), and evaluated the ratio of the band area as  $A_2 : A_3 : A_4 = 1 : 4.5 : 10.4$ . Using this ratio and the phosphorescence lifetimes ( $\tau_2 = 25$  ps,  $\tau_3 = 1.6$  ns and  $\tau_4 = 27$  ns) in Equation S11, the population ratio of the photoexcited dimer, trimer, and tetramer is calculated as  $N_2^0$ :  $N_3^0$ :  $N_4^0 = 92.7$ : 6.5: This result clearly indicates that the dimer is most predominantly excited under 0.8. the present condition (0.038 mol/dm<sup>3</sup>,  $\approx$  270-nm excitation), which is fully consistent with the conclusion based on the concentration dependence of the absorption spectrum in Section 2 of this Electronic Supplementary Information. We note that our recent study of the emission yields of  $[Au(CN)_2]_n$  aqueous solutions revealed a slight tendency that the larger oligomer exhibits the larger radiative rate.<sup>5</sup> This tendency implies that the evaluated population ratio of the photoexcited dimer (92.7 %) is probably a lower limit.

The evaluated population ratio of the photoexcited tetramer is a small but not negligible value (0.8 %). It looks that this evaluation does not accord with the argument based on the steady-state absorption, which indicates that the 0.038 mol/dm<sup>3</sup> solution contains no tetramer in the ground state. This seeming discrepancy is rationalized by the data of our previous time-resolved emission study that was performed for a more highly concentrated solution (0.38 mol/dm<sup>3</sup>)<sup>1</sup> : The emission band characteristic of the tetramer was not observed immediately after photoexcitation, indicating that the ground-state tetramer does not exist even in such a concentrated solution, and the tetramer emission appears with the decay of the trimer emission. Thus, the steady-state emission band observed at 430 nm for the 0.038 mol/dm<sup>3</sup> solution is not generated by photoexcition of the ground-state tetramer, but rather it arises from the excited-state tetramer that is formed by collisions between the excited-state trimer and

ground-state monomer. Using the Debye-Smoulckouski equation, the mean time of collisions between the trimer and the monomer is estimated as 23 ns for the concentration of 0.038 mol/dm<sup>3.1</sup> This collision can be regarded as one of relaxation pathways of the excited trimer, in addition to the ordinary relaxation processes such as radiative and nonradiative transitions, giving the (emission) lifetime of the trimer of 1.6 ns as a total. Thus, the formation yield of the tetramer from the trimer is estimated as  $1.6/23 \sim 0.07.$ This yield is fairly close to the population ratio of the photoexcited trimer and tetramer evaluated above,  $N_4^0 / N_3^0 = 0.8/6.5 \sim 0.12$ ,<sup>6</sup>, which supports that excited-state tetramer is generated by collisions. In contrast, the lifetime of the dimer  $(\tau_2 = 25 \text{ ps})$  is much shorter than the mean time for collisions, meaning that the photoexcited dimer cannot collide with the (ground-state) monomer to form the trimer within its lifetime. Thus, only the dimer and trimer are excited under the present condition, and the population ratio of the photoexcited dimer and trimer is finally evaluated as  $N_2^0$ :  $N_3^0 = 92.7$ : 6.5 = 93.4% : 6.6%.

As discussed above, all the steady-state absorption, emission, and time-resolved emission data consistently show that the excited-state dimer is most predominantly generated with its population ratio larger than 93% when we photoexcite the 0.038 mol/dm<sup>3</sup> solution at  $\approx 270$  nm. The residual minor photoexcited species is the trimer that coexists in the solution, and a portion of the excited-state trimer is converted to the tetramer by collisions. The tetramer and larger oligomers in the ground state do not exist in the solution. These conclusions confirms that we can almost selectively excite the dimer under the optimum condition used in the present study, which is essential for femtosecond time-resolved absorption study of the dimer discussed in the main text.



**Figure S5.** Steady-state emission spectrum of K[Au(CN)<sub>2</sub>] aqueous solution plotted against wavenumber (0.038 mo/dm<sup>3</sup>,  $\lambda_{ex} = 266$  nm), which is calculated from the emission intensity in the wavelength space as  $I(v) = \lambda^2 I(\lambda)$ . Result of the fitting with three Gaussian-shaped functions is shown by the dotted line. The three component bands due to the dimer, trimer, and tetramer are also shown by solid lines.

## 4. Global fitting analysis of the femtosecond timeresolved absorption signals



**Figure S6.** Global fitting of the time-resolved absorption signals of  $[Au(CN)_2]$  in water observed at various wavelengths. The experimental data and the best-fit curves are plotted in black and red, respectively (0.038 mol/dm<sup>3</sup>,  $\lambda_{ex} = 270$  nm).

## Species associated spectra obtained from the global fitting analysis of the transient absorption signals

As mentioned in the main text, the temporal profile of the transient absorption signal was well reproduced by the following tri-exponential function,

$$\Delta A(t,\lambda) = A_1(\lambda)\exp(t/\tau_1) + A_2(\lambda)\exp(t/\tau_2) + A_3(\lambda)\exp(t/\tau_3).$$
(S12)

We obtained the time constants of 0.2 ps, 26 ps and 914 ps for  $\tau_1$ ,  $\tau_2$  and  $\tau_3$ , respectively, by the global fitting, as shown in Figure S6. The obtained parameters for the 400-710 nm region are listed in Table S1. Using these parameters, we obtained species associated spectra as described in the following.

In the present experiment, both the dimer and trimer are contained in the sample solution  $(0.038 \text{ mol/dm}^3)$ . Both of them are excited at 270 nm, generating the initial population of the singlet excited states of [Dimer Singlet (0)] =  $N_2^0$  and [Trimer Singlet (0)] =  $N_3^0$ . Solving the rate equation for the intersystem crossing process under this initial condition, we obtains time-dependent populations of the singlet and triplet excited states of the dimer as

[Dimer Singlet 
$$(t)$$
] =  $N_2^0 \exp(-k_1 t)$ ,

[Dimer Triplet (t)] = 
$$N_2^0 \rho_{12} (\exp(-k_2 t) - \exp(-k_1 t))$$
, (S13)

and those of the trimer as

[Trimer Singlet (t)] =  $N_3^0 \exp(-k_1 t)$ ,

$$[\text{Trimer Triplet } (t)] = N_3^0 \,\rho_{13} \left( \exp(-k_3 t) - \exp(-k_1 t) \right). \tag{S14}$$

Here,  $k_i = 1/\tau_i$ ,  $\rho_{12} = k_1/(k_1 - k_2) = 1.01$ , and  $\rho_{13} = k_1/(k_1 - k_3) = 1.00$ . The intersystem crossing times of the dimer (0.20 ps) and the trimer (0.24 ps) are so close to each other that they are difficult to be distinguished. Thus, we treated the two processes with a common time constant of  $\tau_1 = 0.2$  ps. Also note that the 2.1-ps rising component that was observed for the trimer in the previous study was omitted here for simplicity because the 2.1-ps component due to the minor trimer is not recognized in the present data. Then, the temporal profile of the transient absorption signal can be represented by a sum of the contributions of these species,

 $\Delta A(t,\lambda) = a_s(\lambda) ([\text{Dimer Singlet}(t)] + [\text{Trimer Singlet}(t)])$ 

$$+ a_{d}(\lambda) [Dimer Triplet (t)] + a_{t}(\lambda) [Trimer Triplet (t)].$$
(S15)

Here,  $a_s(\lambda)$ ,  $a_d(\lambda)$ , and  $a_t(\lambda)$  denote the intrinsic absorption intensity of the singlet excited states of both the dimer and trimer, the triplet dimer, and the triplet trimer, respectively, at wavelength  $\lambda$ . Note that we treat the spectra of the singlet dimer and singlet trimer as the sum (i.e., spectrum  $a_s(\lambda)$ ) because they cannot be separated in the present measurement. Substituting (S13) and (S14) into (S15) and then comparing (S15) with (S12), we can relate the intrinsic absorption intensity  $a(\lambda)$  to the amplitudes of the exponential components,  $A(\lambda)$ , that are evaluated experimentally:

$$(N_2^0 + N_3^0) a_{\rm s}(\lambda) = A_1 + A_2 + A_3 , \qquad (S16)$$

$$N_2^0 a_{\rm d}(\lambda) = A_2 / \rho_{12} , \qquad (S17)$$

$$N_{3}^{0} a_{t}(\lambda) = A_{3} / \rho_{13} .$$
(S18)

The relative values of  $a_s$ ,  $N_2^0 a_d$  and  $N_3^0 a_t$  are evaluated at each wavelength by using equations S16 – S18, and their wavelength dependence are shown as the species associated spectra in Figure S7.



**Figure S7**. Species associated spectra obtained from the time-resolved absorption data of  $K[Au(CN)_2]$  aqueous solution (0.038 mol/dm<sup>3</sup>,  $\lambda_{ex} = 270$  nm). red: singlet states of both the dimer and trimer ( $a_s$ ), blue: triplet state of the dimer ( $N_2^0a_d$ ), green: triplet state of the trimer ( $N_3^0a_t$ ).

	$ au_1$	$ au_2$	$ au_3$
(ps)→	0.2	26	916
WL / nm	$A_1$	$A_2$	$A_3$
400	0.00319	0.00574	0.00529
410	0.00179	0.00610	0.00523
420	0.00053	0.00685	0.00548
430	-0.00150	0.00741	0.00564
440	-0.00397	0.00780	0.00552
450	-0.00586	0.00803	0.00546
460	-0.00777	0.00808	0.00541
470	-0.00971	0.00803	0.00546
480	-0.01011	0.00816	0.00563
490	-0.01409	0.00824	0.00591
500	-0.01191	0.00827	0.00635
510	-0.01259	0.00828	0.00701
520	-0.01492	0.00816	0.00769
530	-0.01692	0.00803	0.00829
540	-0.01665	0.00795	0.00870
550	-0.01590	0.00787	0.00887
560	-0.01669	0.00774	0.00887
570	-0.01632	0.00759	0.00872
580	-0.01595	0.00747	0.00848
590	-0.01562	0.00740	0.00821
600	-0.01524	0.00741	0.00784
610	-0.01472	0.00726	0.00743
620	-0.01406	0.00700	0.00706
630	-0.01358	0.00681	0.00673
640	-0.01317	0.00652	0.00648
650	-0.01249	0.00629	0.00620
660	-0.01190	0.00585	0.00605
670	-0.01137	0.00539	0.00599
680	-0.01083	0.00497	0.00588
690	-0.00933	0.00459	0.00580
700	-0.00940	0.00448	0.00584
710	-0.01050	0.00422	0.00587

 Table S1. Fitting parameters for the Global fitting

# 5. Femtosecond time-resolved absorption data of 0.075 mol/dm<sup>3</sup> solution

When the concentration is increased from 0.038 mol/dm<sup>3</sup> to 0.075 mol/dm<sup>3</sup>, additional contribution due to the excited trimer appears in the transient absorption signal. As shown in Figure S8, the 0.075 mol/dm<sup>3</sup> solution exhibits a noticeable 2.1-ps rise due to the trimer, while the 25-ps decay due to the dimer remains the same, ensuring that the 2.1-ps rise arises from the trimer.



**Figure S8.** (a) Femtosecond time-resolved absorption spectra of K[Au(CN)<sub>2</sub>] in 0.075 mol/dm<sup>3</sup> aqueous solution. (b) Temporal traces of the time-resolved absorption signals at 547 nm (red) and 466 nm (blue) (0.075 mol/dm<sup>3</sup>,  $\lambda_{ex} = 270$  nm).

## 6. Optimized structure of $[Au(CN)_2]_n$ in the $T_1$ state

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X Y Z		
		-1.345898 0.064985 -0.015032		
2	79	1.346237 -0.065048 0.012591		
3	6	-1.580052 -1.370909 -1.356825		
4	6	-1.353983 1.511587 1.332934		
5	6	1.298446 -1.439658 1.432659		
6	6	1.634977 1.297530 -1.394211		
7	7	-1.657423 -2.226815 -2.155362		
8	7	-1.282478 2.369479 2.130009		
9	7	1.190604 -2.251760 2.272516		
10	7	1.745993 2.111052 -2.232089		

## 6.1. Optimized structure of $[Au(CN)_2]_2$ in the T<sub>1</sub> state

SCF-energy :

-642.058304857

Hartree



Figure S9. Optimized structure of triplet excited-state dimer  $[Au(CN)_2^{-}]_2$ .

Center	Atomic	Coordi	Coordinates (Angstroms)			
Number	Number	Х	Y	Z		
	79	1 363351	0.001838			
2	79	4 214930	-0.002889			
3	79	-1 367620	0.008987	0.005865		
4	6	1.380152	-1 446705	-1.352382		
5	6	1.388126	1 443671	1.354135		
6	6	4 340213	-1 405541	1 393777		
7	6	4.040210	1 392239	-1 /00832		
8	6	-1 381064	-1 205211	1.570616		
0	6	-1 387720	1.205211	-1 556211		
10	7	1.007729	-2 202110	-2 1500211		
10	7	1.070449	-2.303110	-2.150955		
10	1	1.380279	2.290912	2.100007		
12	/	4.399008	-2.235495	2.21/118		
13	/	4.409397	2.220562	-2.225735		
14	7	-1.374353	-1.919811	2.498194		
15	7	-1.383515	1.945208	-2.480947		
16	79	-4.215442	-0.006596	-0.003397		
17	6	-4.333893	-1.562261	-1.225016		
18	6	-4.341338	1.549228	1.216825		
19	7	-4.379630	-2.484975	-1.943832		
20	7	-4.387706	2.472183	1.935316		

## 6.2. Optimized structure of $[Au(CN)_2]_4$ in the T<sub>1</sub> state

SCF-energy: -1284.36242460 Hartree



Figure S10. Optimized structure of triplet excited-state tetramer [Au(CN)<sub>2</sub><sup>-</sup>]<sub>4</sub>.

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- 6. A rise component expected for the time profile of the tetramer emission due to the collision was ignored because its contribution to the emission yield is small (~ 5 %)