

Amplified Spontaneous Emission from the Film of Poly(aryl ether) Dendrimer Encapsulating Excited-State Intramolecular Proton Transfer Dye

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Nonresonant exponential amplification of the excited-state intramolecular proton transfer (ESIPT) emission has been investigated with the film of ESIPT dendrimer (QG2) by pico- and femtosecond laser experiments. The intrinsic four-level nature of ESIPT and the reduced concentration quenching by dendritic effect made QG2 film an optical gain medium with the threshold intensity lower than $20 \mu\text{J}/\text{cm}^2/\text{pulse}$. The characteristics of emission amplification are discussed in terms of the amplified spontaneous emission (ASE) related with ESIPT.

Introduction

Highly fluorescent organic materials including small laser dyes and conjugated polymers have been intensively investigated as an active gain medium for optically pumped solid lasers.¹ Among various kinds of fluorescent dyes, the one based on the excited-state intramolecular proton transfer (ESIPT) has a distinct advantage for stimulated emission because it possesses an intrinsic four-level photocycle scheme implemented by the enol (E)–keto (K) phototautomerization ($\text{E} \rightarrow \text{E}^* \rightarrow \text{K}^* \rightarrow \text{K} \rightarrow \text{E} \rightarrow \dots$). However, in common with conventional laser dyes, the most serious limitation of the ESIPT system to actual applications is that optical gain is difficult to achieve because of the severe concentration quenching of the proton-transferred keto emission. In fact, ESIPT molecules such as hydroxyphenylbenzazoles had to be studied under considerably dilute conditions for proton-transfer laser within the cavity structure.^{2,3}

Very recently, we reported highly concentrated but still ESIPT-active solid media, that is, films of semirigid polyquinoline and poly(aryl ether) dendrimers possessing phototautomerizable quinoline as a repeating unit and core, respectively.^{4,5} In this work, we report exponential amplification and gain narrowing of ESIPT emission from the nonresonant structure, that is, from the neat film of the second-generation dendrimer, QG2 (see Figure 1), under high excitation intensity. Emission amplification without cavity is normally observed in efficient optical gain media above threshold excitation intensity. The underlying mechanism is still under debate and has been assigned to various physical origins including amplified spontaneous emission (ASE) by stimulated emission,^{6–9} or dipole-coupled cooperative emission such as superradiance (SR) or superfluorescence (SF).^{10–13} Nonresonant amplification in organic media has mostly been observed from thin films of conjugated polymers or their energy-transferring blends.^{6–14} This is because the conjugated polymers are capable of optical gain even in the concentrated film due to a virtual four-level scheme

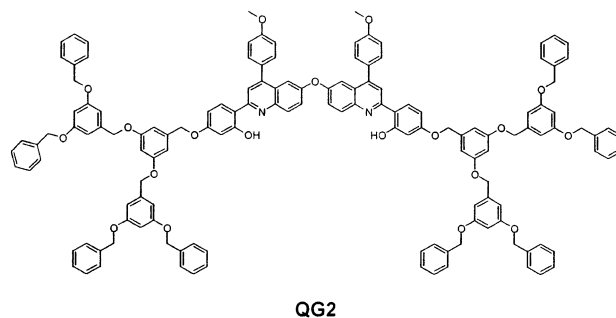


Figure 1. Chemical structure of QG2.

induced by large vibronic relaxation along the conjugated backbone. In the case of small laser dyes, however, exponential amplification without cavity is a rare case and a high level of dilution and site isolation are demanded at the expense of active chromophore density to suppress significant concentration quenching.^{15,16}

As shown in Figure 1, QG2 can be regarded as a class of dendritically isolated ESIPT dye. It is specifically noted that the active chromophore content in the neat film of QG2 is fairly high (32.5% of core and 67.5% of dendron shell in total weight). Considering the difficulties in achieving net gain with conventional laser dyes, the origin of the nonresonant emission amplification from QG2 film is most probably related to the ESIPT nature and the dendritic effect of QG2. Here, we investigated the nonresonant emission amplification characteristics from the QG2 film by pico- and femtosecond laser experiments to elucidate the photophysical nature and the amplification mechanism related to ESIPT.

Experimental Section

The detailed synthetic procedure of QG2 and its optical properties including picosecond kinetics were reported in our previous work.⁵ QG2 film for picosecond lasing experiments was prepared by spin casting onto a glass slide from 1 wt %

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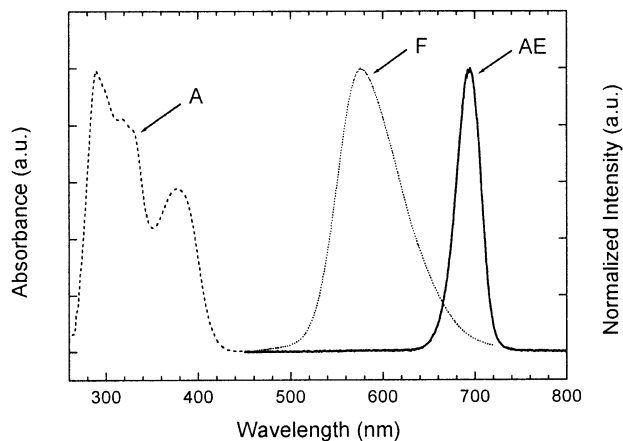


Figure 2. Absorption (A), ordinary orange fluorescence (F), and amplified red emission (AE) spectra of QG2 spun film.

dichlorobenzene solution after filtration through a 0.5 μm syringe filter. The pump source was the third harmonic (355 nm, 10 Hz) of a passively/actively mode-locked Nd:YAG laser (B. M. industries, 5022 D.P.S. DP10) with the pulse duration of 30 ps, and the excitation area of a circular shape was 0.79 cm^2 . The pump beam was directed normal to the film surface through the glass substrate to minimize simultaneous exposure to light and oxygen. The amplified emission from the film edge was recorded in air at room temperature with a photonic multichannel analyzer (PMA, Hamamatsu Photonics) system with a dual MOS photodiode array (C6140). The emission anisotropy was obtained by measuring the emission spectra from the film normal and the edge simultaneously with the same measurement system. The emission kinetic profiles were measured using an imaging spectrograph (Hamamatsu, C5094) and a streak scope (Hamamatsu, C2830) with a high-speed streak unit (Hamamatsu, M2547). The femtosecond pump–probe measurement was carried out with the drop-cast blend film of QG2 in commercial polycarbonate (30 wt %) for film toughness. The specimen was excited with the second harmonic (400 nm, 80 $\mu\text{J}/\text{pulse}$, 10 Hz) of a femtosecond Ti:sapphire laser (800 nm, 200–250 fs pulse duration) with a regenerative amplifier and a double path amplifier pumped with the second harmonic of a Nd:YAG laser. A probe white light was obtained by focusing the residual 800 nm pulse after the second harmonic generation by a BBO crystal into a cell of $\text{D}_2\text{O}/\text{H}_2\text{O}$ (2:1) mixture. The transient absorption spectra were recorded with the same PMA system used for the picosecond emission amplification.

Results and Discussion

In our previous work, the core of QG2, that is, nondendritic quinoline chromophore in itself, was found not to suffer significantly from concentration quenching in the vacuum-evaporated neat film, contrary to the conventional ESIPT dyes.¹⁷ The second generation poly(aryl ether) dendron was also found to further reduce the quenching effect to give more enhanced emission efficiency in the film state by site isolation of the ESIPT dye.⁵ Spin-cast film of QG2 (480 nm thick) showed typical ESIPT characteristics, that is, UV-region absorption and orange emission without any overlap in between, as shown in Figure 2. This abnormally large Stokes' shift (~ 200 nm) is ascribed to the different absorbing and emitting species in this quinoline-based ESIPT dye.⁴ The absorbing species is the enol tautomer (E), which preferably exists in the ground state. Photoexcited enol (E^*) decays rapidly to the more stable excited keto form (K^*) via ESIPT because the latter is more stable than

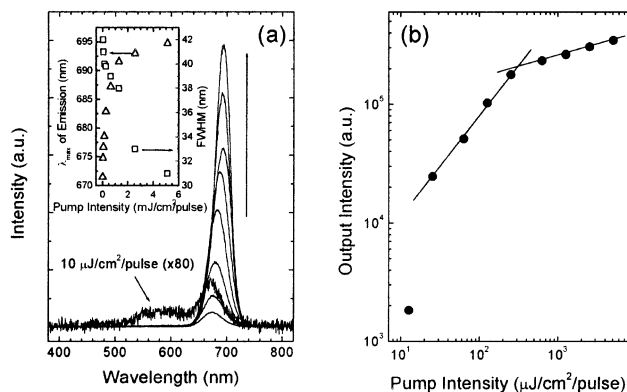


Figure 3. Emission spectra (a) of QG2 spun film (480 nm thick). The excitation intensity increases from 10 to 5100 $\mu\text{J}/\text{cm}^2/\text{pulse}$ in the order indicated by the bold arrow. The inset shows the traces of λ_{max} and fwhm. Panel b shows the dependence of the integrated emission intensity on the excitation intensity.

the former. The K^* state, the emitting species, then decays radiatively to K, which is subsequently followed by reverse proton transfer to E to complete a cycle. The unique orange emission of QG2 that is greatly red-shifted (~ 200 nm) from the ground-state absorption can thus be assigned as the proton-transferred keto emission. The complete absence of enol emission, which is supposed to appear in the blue region, indicates that ESIPT is a major decay route of E^* state rather than normal fluorescence. Actually, proton transfer in QG2 film is very fast, as measured to be 29 ps by picosecond fluorescence kinetics.⁵ It is speculated that the effective and fast ESIPT in this dendritic solid film originates from the stronger and energetically more favored intramolecular hydrogen bond in the film state where torsional motion is virtually frozen. In fact, it is observed that the fluorescence of QG2 solution in any good solvents is very weak but that of spin-cast film is quite strong.

When the QG2 film was excited by a 355 nm picosecond laser pulse with circular excitation area, the orange keto emission was amplified to the intense and narrow red band. Figure 3 shows spectral evolution depending on the pump intensity, where the emission was collected from the film edge. At low intensity of 10 $\mu\text{J}/\text{cm}^2/\text{pulse}$, a new emission band in the red region appears besides the ordinary orange band at 576 nm, where the total intensity is not amplified yet (Figure 3a). When the pump intensity is gradually increased, only the red band is markedly amplified such that the ordinary orange band seems ignorable. As shown in the inset of Figure 3a, the amplification gain is gradually moved to longer wavelength and narrowed. In the high pumping region, the traces of the peak wavelength (λ_{max}) and the full width at half-maximum (fwhm) are asymptotically approaching 695 and 31 nm, respectively. The integrated emission intensity shows hyperlinear dependency on the pump intensity in the range of 20–300 $\mu\text{J}/\text{cm}^2/\text{pulse}$ (Figure 3b), indicating that this pumping range is already above the threshold intensity. Thus, it can be roughly mentioned that the threshold for amplification is lower than 20 $\mu\text{J}/\text{cm}^2/\text{pulse}$, indicative of easy population inversion by the intrinsic four-level nature of ESIPT. Similar to the pump intensity dependencies of λ_{max} and fwhm, the emission intensity seems to level off above 300 $\mu\text{J}/\text{cm}^2/\text{pulse}$, implying gain saturation. As a result, QG2 film shows peculiar broad-band gain amplification of ca. 30 nm that is at odds with the conventional gain amplification with fwhm less than 10 nm.

To understand the photophysical properties of QG2 film, femtosecond pump–probe spectroscopic measurement under amplification condition was carried out by varying the delay

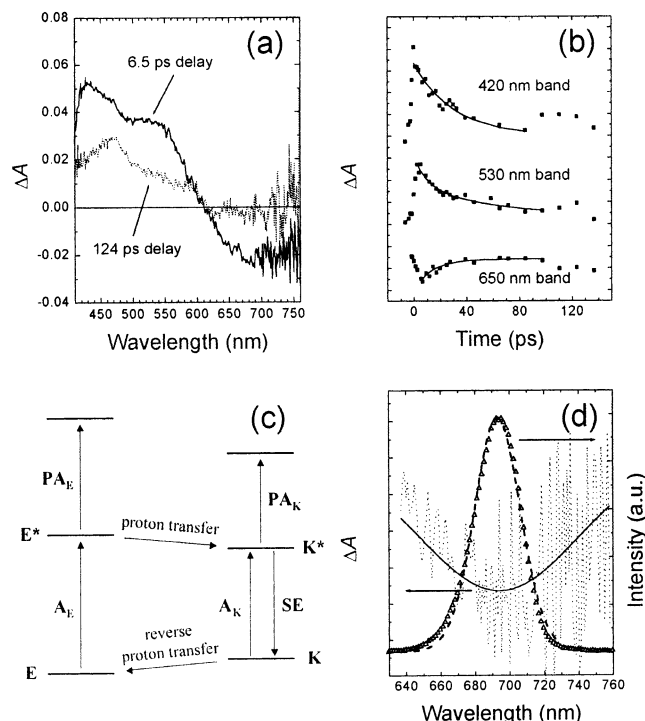


Figure 4. Transient absorption spectra (a) at two different delay times of probe incident, (b) temporal profiles of three characteristic bands, (c) simplified optical transitions in QG2 film, and (d) gain spectrum (dotted line), its Gaussian line shape function (solid line), and amplified emission spectrum (open triangle). The emission fitting curve (dashed line) was obtained with the assumption of ASE.

time of probe incidence. The obtained transient spectroscopic bands are expressed by transient absorption change (ΔA), as shown in Figure 4a. Just after excitation (6.5 ps delay), two positive photoinduced absorption (PA) bands at 420 and 530 nm and one negative transient absorption band at ca. 690 nm were observed. After these bands decayed (124 ps delay), a new PA band appeared at 470 nm. The early negative band is well-accordant with the amplified emission (AE) in Figure 2 and can be assigned as optical gain by stimulated emission (SE), where the delayed probe beam stimulates the proton transferred K^* into SE. Note that the formation of K^* after ESIPT leads to a population inversion because K does not exist initially.

Figure 4b shows the kinetic profiles of the early bands, on the basis of which the photophysical scheme is proposed and shown briefly in Figure 4c. The 420 nm PA band decays exponentially with a time constant (τ) of 30 ps. This kinetics is almost the same as that of ESIPT (29 ps) occurring in E^* .⁵ This kinetic accordance makes it rational to assign this PA band as the absorption of E^* toward higher excited states (PA_E). The decay of the 530 nm PA band was best fitted by a double exponential function with τ of 10 ps (44%) and 70 ps (56%), while the SE band monitored at 650 nm showed single-exponential kinetics ($\tau = 12$ ps). Good accordance between SE decay and the fast decay component of 530 nm PA strongly implies that the two processes would originate from the same species, that is, K^* . Consequently, the PA band at 530 nm can be assigned as the absorption of K^* (PA_K). There may be a small absorption loss in the excited state due to slight overlap between this PA_K band and the keto emission observed in the static spectrum (peaking at 576 nm), to result in the red-shifted net gain as a sum. The reason for gain shift with increasing pump intensity in Figure 3a is not clear but may also be found in the competition of these two bands depending on the pump intensity. The slow component of the 530 nm band is probably

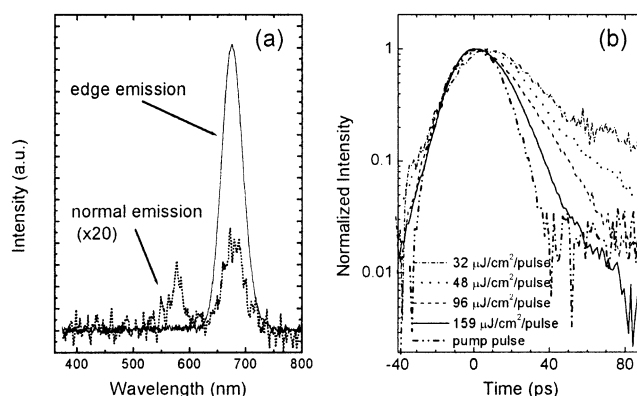


Figure 5. Emission spectra (a) from the normal and the edge sides of QG2 film, excited with $63 \mu J/cm^2/pulse$ and (b) picosecond pump pulse and emission kinetics at various pump intensities.

due to the complicated influence of the near-positioned 470 nm band formed later. The rise in the profiles of 420 and 530 nm bands after 80 ps is a clear influence of the 470 nm band. This 470 nm band can be understood as the absorption of K (A_K), considering that the delayed rise means the formation of K after K^* decay. It is noteworthy that the A_K band is shown only in the transient absorption spectrum, indicating that almost all of the keto form decays to the enol form in the ground state. The decay time of K to E seems to be fairly long such that the kinetics is hard to analyze with the probe delay up to 650 ps. The longer lifetime of K than that of K^* , which possibly leads to the population stack in the K state, may be a major reason for the gain saturation shown in Figure 2.¹⁸

Figure 4d shows the theoretical prediction of gain amplification, simply obtained by taking the ASE mechanism into account. If we assume that the spontaneously emitted photons are amplified by stimulated emission as they propagate through the gain medium by waveguiding, we can use the following simple argument. The wavelength-dependent intensity function of amplified emission, $I_{AE}(\lambda)$, is proportional to the gain line shape function, $I_0(\lambda)$, and an exponential amplification factor given by $\exp[g(\lambda)z]$, where $g(\lambda)$ is the gain coefficient and z is a propagation length.¹⁸ As an approximation, we fit the optical gain in Figure 4a as a Gaussian curve (straight line in Figure 4d) and simply obtain $I_0(\lambda)$ and $g(\lambda)$ by multiplication of the Gaussian function with some factor. Finally, we can fit the amplified emission curve in Figure 3 using the obtained $I_{AE}(\lambda)$. The fitting result (dashed line in Figure 4d) matches closely with the experimental one, indicating that the amplification of QG2 film can be explained in terms of ASE. Actually, the amplification in QG2 film is strongly influenced by waveguiding along the film plane, as shown by the emission anisotropy detected from the normal and edge side of the film simultaneously (Figure 5a). The gain amplification only in the edge direction indicates that only the emission guided within the excited region of the film can be amplified by stimulated emission, strongly supporting the above consideration of ASE.

The picosecond kinetics of the amplified emission in Figure 5b gives a direct evidence for the proton-transfer ASE. The delayed rise in all of the profiles indicates that the amplified emission occurs after ESIPT. The emission profiles also show ultrafast decays compared with the spontaneous emission lifetime (200 ps)⁵ and are well-fitted by a single-exponential decay function. The obtained emission lifetime gradually decreases from 25 to 12 ps with increasing excitation intensity. The ultrashort decay time and its steady decrease with increasing

excitation intensity are suitably explained only by the excited-state population depletion model utilizing the ASE mechanism.^{7,8,18}

Conclusions

Nonresonant emission amplification from the film of a poly-(aryl ether) dendrimer (QG2) was investigated by pico- and femtosecond spectroscopy. QG2 film was found to have optical net gain in the spectral region of proton-transfer emission due to easy population inversion by the four-level nature of ESIPT and ignorable absorption loss. It has been concluded that the emission amplification from the QG2 film is proton-transfer ASE by stimulated emission within gain medium.

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