

Evidence for the coexistence of two different mechanisms for the occurrence of anti-Kasha $S_2(1^1B_u)$ fluorescence from α,ω -diphenylpolyenes

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Fluorescence, fluorescence excitation, and absorption spectra have been measured for diphenylpolyenes with the polyene double bond number (n) from three to seven in solvents with different polarizabilities at room temperature. These polyenes exhibit anti-Kasha $S_2(1^1B_u)$ fluorescence beside conventional $S_1(2^1A_g)$ fluorescence in room temperature solution. It is shown that there are two different mechanisms for occurrence of the $S_2(1^1B_u)$ fluorescence of diphenylpolyenes. S_2 fluorescence occurs through the thermal population of the S_1 state for the shorter diphenylpolyenes ($n=3$ and 4), while it occurs as prompt S_2 fluorescence due to inefficient $S_2 \rightarrow S_1$ internal conversion for the longer diphenylpolyenes ($n=6$ and 7). With diphenyldecapentaene ($n=5$), S_2 fluorescence based on both mechanisms is observed depending on the polarizability of the solvent used. The present results provide deeper insight into the mechanism for the occurrence of anti-Kasha S_2 fluorescence of polyenes. © 2004 American Institute of Physics. [DOI: 10.1063/1.1791155]

I. INTRODUCTION

Fluorescence of organic molecules originates normally only from their lowest excited singlet (S_1) state, irrespective of the photon energy used for the excitation. The generalization of this observation is referred to as Kasha's rule.¹ Although Kasha's rule applies to almost all emissive molecules, there are a few exceptions. Emission from higher excited singlet states, S_2 , S_3 , S_4 , ..., is often called "anti-Kasha emission" in contrast to the normal emission which obeys Kasha's rule.

It has passed over 30 years since the discovery of the one-photon forbidden $S_1(2^1A_g)$ state of linear polyenes.^{2,3} It is now well established that for diphenylpolyenes with n over 3 the 2^1A_g state is S_1 and that the one-photon allowed 1^1B_u state is S_2 ,⁴⁻⁷ although for diphenylbutadiene ($n=2$) these states are nearly isoenergetic so that the apparent order can differ in different experiments.⁸ Recently it was revealed that α,ω -diphenylpolyenes [$\text{Ph}-(\text{CH}=\text{CH})_n-\text{Ph}$] with n from five to seven exhibit weak anti-Kasha $S_2(1^1B_u)$ fluorescence beside the $S_1(2^1A_g)$ fluorescence.⁹⁻¹¹ Thus, it is of interest to investigate the spectroscopic properties of a series of diphenylpolyenes in more detail, since we can obtain information on the interaction of the two excited states directly through the measurement of dual fluorescence. Determination of mechanism for the occurrence of the anti-Kasha emission is of importance with respect to the molecular nonradiative transition theory as well as to the excited-state dynamic behavior of organic molecules. Linear polyenes of other types such as carotenoids also are known to show anti-Kasha S_2 fluorescence.¹²⁻¹⁴ Detailed information on the electronic

structure of conjugated linear polyenes is fundamental to understand complicated processes of charge transport in conducting polymers as well as energy transfer in biological systems.¹⁵

In the present work, fluorescence, fluorescence excitation, and absorption spectra have been measured for diphenylpolyenes with n from three to seven in solvents with different polarizabilities at room temperature. Evidence is given for the coexistence of two different mechanisms for the occurrence of the S_2 fluorescence from diphenylpolyenes. Although $S_2(1^1B_u)$ fluorescence is known to occur through thermal population of the S_1 state for shorter diphenylpolyenes ($n=3$ and 4; DP3 and DP4, respectively),¹⁶⁻¹⁹ it occurs as prompt fluorescence due to inefficient internal conversion from S_2 to S_1 for longer diphenylpolyenes ($n=6$ and 7; DP6 and DP7, respectively). With diphenyldecapentaene ($n=5$; DP5), the S_2 fluorescence based on both mechanisms is observed: In solvents of low polarizability S_2 fluorescence occurs promptly due to inefficient $S_2 \rightarrow S_1$ internal conversion, but with increasing solvent polarizability the decrease in the S_1 - S_2 energy separation leads to the thermal population of the S_2 state for DP5. In both mechanisms the S_2/S_1 fluorescence-intensity ratio depends significantly on solvent polarizability which controls the S_1 - S_2 energy separation. These observations are interpreted on the basis of the coupling strength between the S_1 and S_2 states, i.e., the intensity borrowing, which depends mainly on the S_1 - S_2 energy separation for DP6 and DP7, but are interpreted on the bases of thermal population of the S_2 state for DP3 and DP4. The present results provide deeper insight not only into the polyene electronic state, but also into the mechanism for the occurrence of the anti-Kasha emission of organic molecules.

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II. EXPERIMENT

Diphenylhexatriene ($n=3$, DP3) and diphenyloctatetraene ($n=4$, DP4) obtained from Aldrich, USA were recrystallized repeatedly from hexane. Diphenyldecapentaene ($n=5$, DP5), diphenyldodecahexaene ($n=6$, DP6) and diphenyltetradecaheptaene ($n=7$, DP7) were synthesized according to the procedure reported by Spangler *et al.*²⁰ and recrystallized from a mixture of dimethylformamide and toluene. Longer diphenylpolyene samples were found to contain trace amounts of shorter and more fluorescent diphenylpolyenes as impurities, which were removed by repeated recrystallizations. Special care was taken in the purification of DP5, since the S_2 fluorescence origin of DP5 matches almost exactly the S_1 fluorescence origin of highly fluorescent DP4. It was confirmed that the measured S_2 fluorescence of DP5 does not originate from DP4, based on the measurements of the excitation spectrum, fluorescence spectral shape, as well as on the repeated purification—emission measurement cycles. Carbon tetrachloride, *n*-hexane, and carbon disulfide obtained from Wako Pure Chemicals, Japan, were used as received, after we confirmed that these solvents contained no impurities that were emitted under our experimental conditions. All these solvents were of spectroscopic grade.

Absorption spectra were measured with a Shimadzu UV-2550 spectrophotometer, and emission and excitation spectra were measured with a Spex Fluorolog-3 (Model 21-SS) spectrophotometer, equipped with a double-grating excitation monochromator, a high-pressure 450-W Xenon lamp as an excitation-light source, and a photomultiplier tube (Hamamatsu R928-P) in an electric-cooled housing operated in photon-counting mode. For most of the emission measurements square 10 mm path length quartz cells were used. Raman and Rayleigh scattering light from the solvents were subtracted from the measured emission spectra. Special care was taken to measure the emission spectra of the samples, and Raman and Rayleigh scattering spectra of the solvents under exactly the same conditions. Sample solution in a cell was changed using a filtered injection without replacing the cell in the cell holder. It was confirmed that the excitation spectrum of all the measured emission agrees well with the corresponding absorption spectrum.

Fluorescence spectra were corrected for the spectral sensitivity of the detection system by comparing the measured spectrum with the real spectrum using *N,N*-dimethylnitroaniline as a standard which shows emission ranging from 12 000 to 22 000 cm^{-1} in a hexane-benzene mixture.²¹ Fluorescence spectra ranging from 18 000 to 25 000 cm^{-1} were corrected using quinine in sulfuric acid as a standard. Excitation spectra were corrected for the spectral intensity distribution of the exciting light with an aqueous solution of rhodamine B as a quantum counter. Emission spectral data were fitted by a least-square procedure.

III. RESULTS AND DISCUSSION

Figure 1 shows absorption and corrected fluorescence spectra of diphenylpolyenes (DP3–DP7) in CCl_4 at room temperature. The measured emission spectra are composed of blue and red spectra: The blue spectra are assigned to

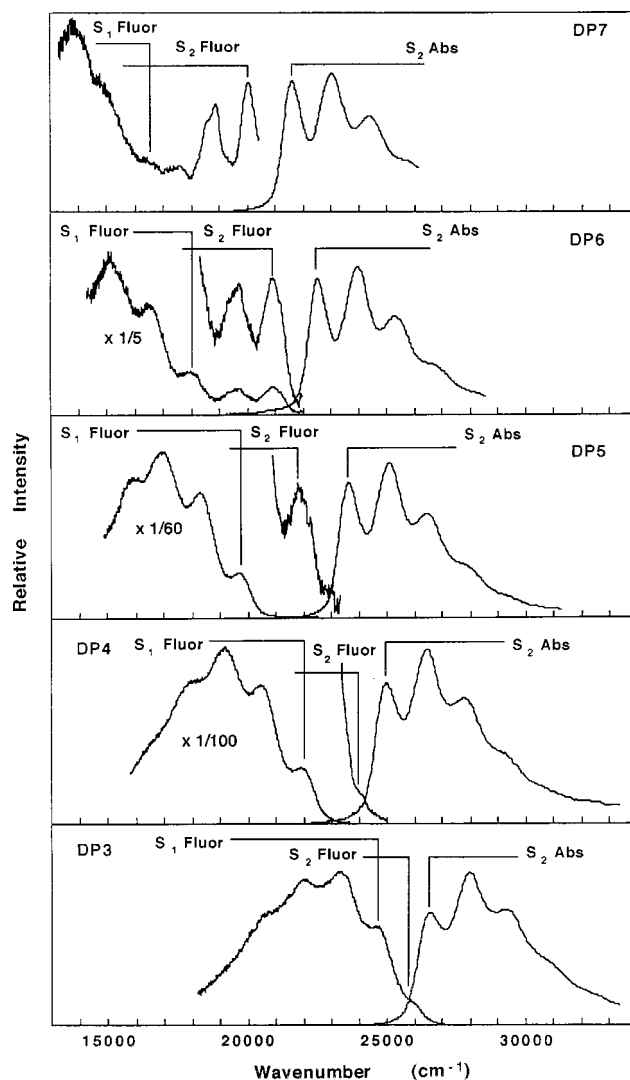


FIG. 1. Fluorescence (left) and absorption spectra (right) of diphenylpolyenes, DP3 (bottom) to DP7 (top), in CCl_4 at room temperature.

fluorescence from the S_2 (1^1B_u) state, as is indicated by a good mirror-image relationship between the fluorescence and the $S_0 \rightarrow S_2$ absorption bands, while the red spectra are assigned to the fluorescence from the S_1 (2^1A_g) state. With DP3, DP4, and DP5, the S_2 fluorescence is comparatively weak, so that it is observed only as a blue shoulder overlapping the onset of the strong S_1 fluorescence. Further, the solubilities and fluorescence quantum yields of longer diphenylpolyenes are extremely low, so that the fluorescence spectra of these molecules are somewhat noisy. It was confirmed that the excitation spectra obtained by monitoring either the S_1 or the S_2 fluorescence emissions agree with the absorption spectra for all the molecules. One can see clearly in Fig. 1 that the relative intensity of the S_2 fluorescence depends strongly on the polyene chain length. In order to treat the observed spectral intensity ratios quantitatively, only the second bands of the S_1 fluorescence and the first band of the S_2 fluorescence spectrum were reproduced using fitted Gaussians, and the intensities of the reproduced bands are treated as the S_1 and S_2 fluorescence intensities (I_1 and I_2 , respectively). An example of a fitted spectrum is shown in Fig. 2

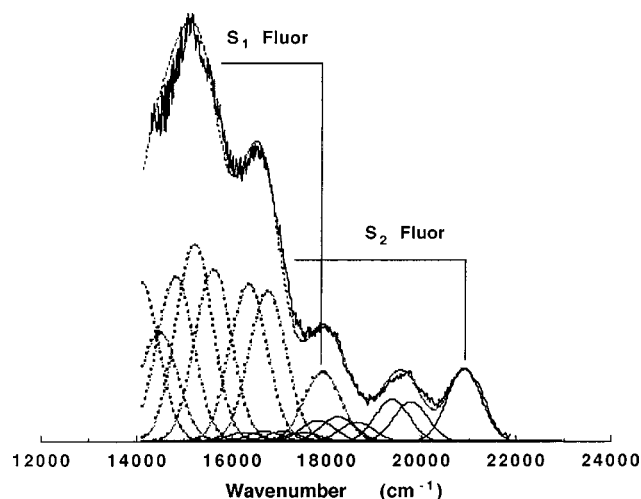


FIG. 2. Observed (solid-line spectrum) and fitted fluorescence spectrum (broken-line spectrum) for DP6 in CCl_4 at room temperature. Used functional forms are indicated by solid-line Gaussians (S_2 fluorescence) and dotted-line Gaussians (S_1 fluorescence).

for DP6 in CCl_4 at room temperature. The spectral change shown in Fig. 1 is well visualized when the S_2 to S_1 fluorescence intensity ratio, I_2/I_1 , is plotted as a function of n (Fig. 3). The value for I_2/I_1 shows a minimum at $n=5$ and 4, respectively, in CS_2 and in CCl_4 at room temperature.

In order to analyze the relative fluorescence intensities systematically, the emission spectra of the diphenylpolyenes were measured in solvents with different polarizabilities. It is well known that the S_2 energy of polyenes shifts to lower energy as the solvent polarizability is increased, while the S_1 energy is almost unchanged. The dependence of the S_1 - S_2 energy separation ΔE on the solvent polarizability has been well rationalized for diphenylpolyenes.²² In Figs. 4(a)–4(c), respectively, we show absorption and corrected fluorescence spectra of DP6, DP5, and DP4 in solvents with different

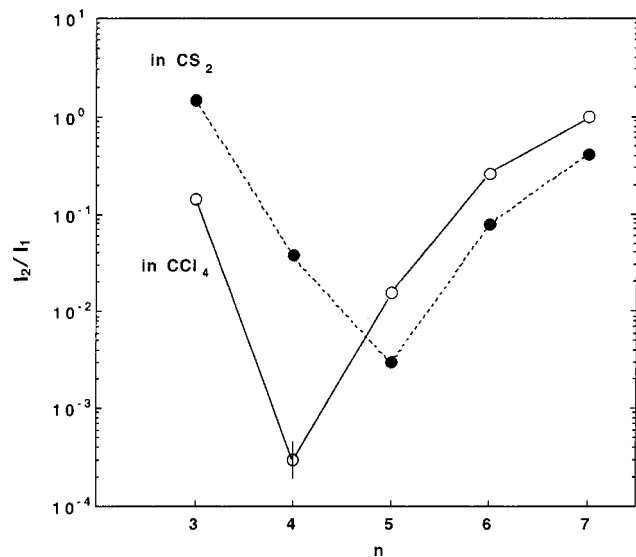


FIG. 3. The I_2/I_1 intensity ratio plotted against the polyene double bond number n of diphenylpolyenes in CCl_4 (open circles) and in CS_2 (closed circles) at room temperature.

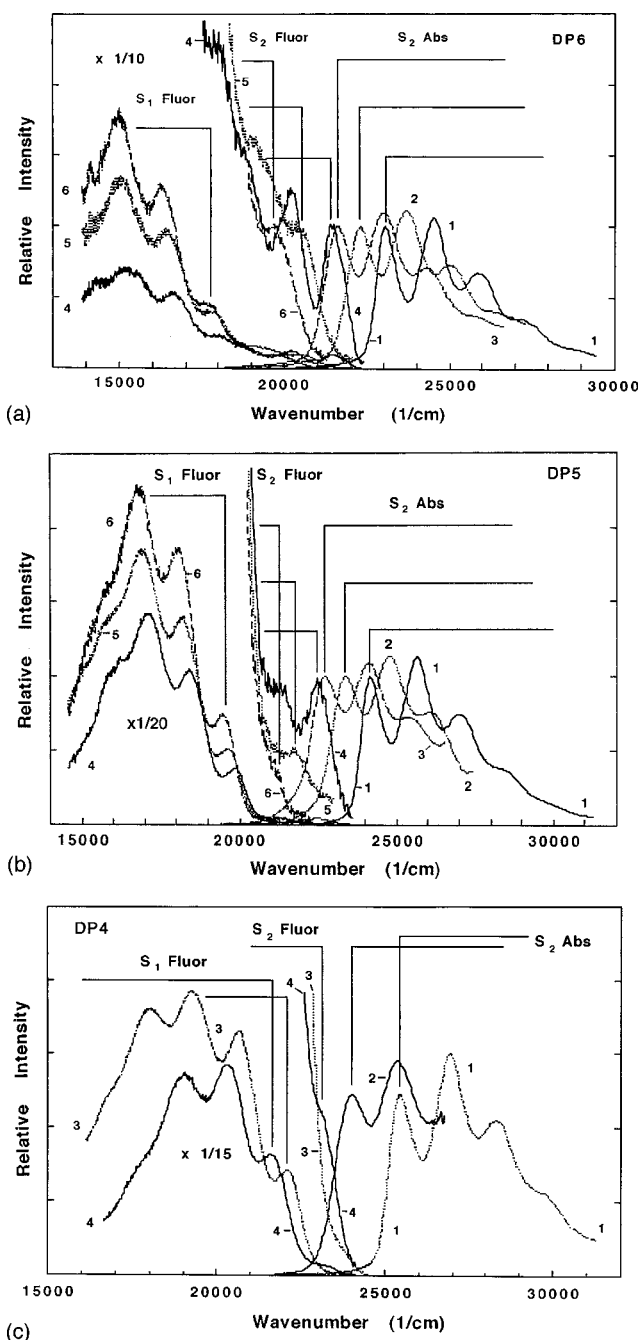


FIG. 4. (a) Absorption (1, 2, and 3) and corrected fluorescence spectra (4, 5, and 6) of diphenyldecahexaene (DP6) in solvents with different polarizabilities at room temperature: In n -hexane (1 and 4), a n -hexane- CS_2 (1:1) mixture (2 and 5), and CS_2 (3 and 6). (b) Absorption (1, 2, and 3) and corrected fluorescence spectra (4, 5, and 6) of diphenyldecaheptaene (DP5) in solvents with different polarizabilities at room temperature: In n -hexane (1 and 4), a n -hexane- CS_2 (1:1) mixture (2 and 5), and CS_2 (3 and 6). (c) Absorption (1 and 2) and corrected fluorescence spectra (3 and 4) of diphenyloctatetraene (DP4) in solvents with different polarizabilities at room temperature: In n -hexane (1 and 3) and CS_2 (2 and 4).

polarizabilities at room temperature. It is clearly seen in Figs. 4(a)–4(c) that the relative intensity of the S_1 fluorescence to the S_2 fluorescence changes significantly depending on the solvent. However, the behavior of the fluorescence intensity upon changing the solvent polarizability for DP4 differs from those for DP5 and DP6. The relative S_2 fluorescence inten-

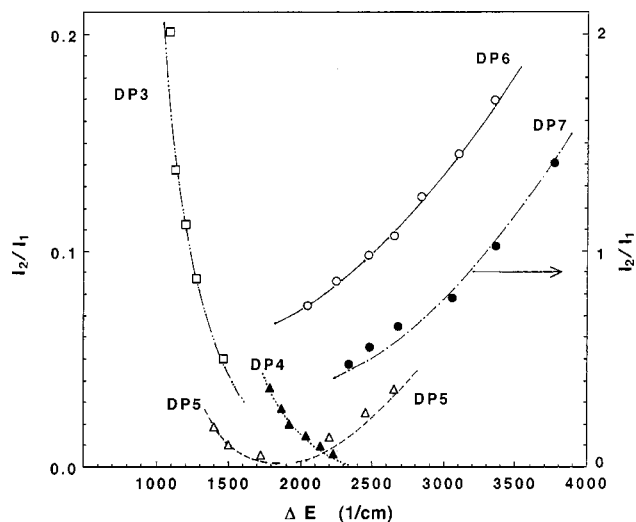


FIG. 5. The I_2/I_1 intensity ratio plotted against the S_1 - S_2 energy gap ΔE for DP3, DP4, DP5, DP6, and DP7 in solvents with different polarizabilities at room temperature.

sity increases for DP4, while it decreases for DP5 and DP6 both with increasing the solvent polarizability.

In Fig. 5 the relation between the S_2/S_1 fluorescence-intensity ratio, I_2/I_1 , and the S_2 - S_1 energy separation ΔE is presented, where the energy difference between the apparent S_1 and S_2 fluorescence origins is taken as the value for ΔE . One can see clearly in Fig. 5 that the ratio I_2/I_1 decreases significantly with increasing ΔE for DP3 and DP4, while it increases monotonically with increasing ΔE for DP6 and DP7. With DP5 two different behaviors of the fluorescence intensity ratio were observed depending on ΔE : The ratio I_2/I_1 decreases for ΔE below about 2000 cm^{-1} , but it increases for ΔE over about 2000 cm^{-1} both with increasing ΔE . These observations indicate that the mechanism for the occurrence of the S_2 fluorescence of DP6 and DP7 is different from that of DP3 and DP4.

With DP3 and DP4 S_2 fluorescence is known to occur as a result of thermal repopulation from the S_1 state.¹⁶⁻¹⁹ However, the S_2 fluorescence of DP6 and DP7 is prompt fluorescence that occurs as a result of inefficient internal conversion from S_2 to S_1 due to a large energy separation between the two excited states.²³ In the former mechanism, i.e., the one for DP3 and DP4, the S_2/S_1 intensity ratio (I_2/I_1) can be expressed by

$$I_2/I_1 \sim \exp(-\Delta E/kT), \quad (1)$$

where k is the Boltzmann constant and T is the absolute temperature.^{17,18} Thus, at a given temperature the ratio I_2/I_1 increases with decreasing ΔE , which depends strongly on the solvent polarizability. It has already been demonstrated for DP3 and DP4 that I_2/I_1 obeys Eq. (1) when the temperature is changed.¹⁸ On the other hand, in the latter mechanism, i.e., the one for DP6 and DP7, the ratio I_2/I_1 can be expressed by

$$I_2/I_1 \sim \Delta E^2, \quad (2)$$

since the S_1 state is considered to borrow oscillator strength through the interstate coupling with S_2 ,^{11,24} and since the

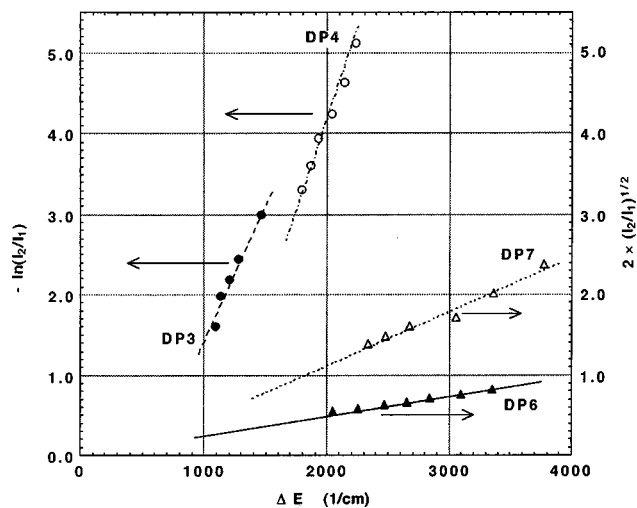


FIG. 6. Values for $-\ln(I_2/I_1)$ (for DP3 and DP4) or $(I_2/I_1)^{1/2}$ (for DP6 and DP7) plotted against ΔE at room temperature.

rate constant for the internal conversion from S_2 is reported to be almost invariant for diphenylpolyenes with n from 3 to 7.²⁵ It has been demonstrated recently for DP7 that the observed S_2/S_1 intensity ratio (I_2/I_1) is expressed approximately by $I_2/I_1 \sim \Delta E^2/K^2$, where K is the coupling constant between the S_1 and S_2 states.^{11,24} This treatment is somewhat different from that for carotenoids, for which the change of I_2/I_1 has been interpreted by enhancement of the S_2 to S_1 internal conversion rate with decreasing ΔE .¹³ The plots in Fig. 6 show clearly the difference between the two mechanisms. That is, the ratio I_2/I_1 is almost proportional to $\exp(-\Delta E/kT)$ for DP3 and DP4 at a given temperature, while it is almost proportional to ΔE^2 for DP6 and DP7. Further, S_2 fluorescence based on both mechanisms is observed for DP5 whose S_1 - S_2 energy separation ranges from 2000 to 3500 cm^{-1} depending on the solvent used (see Fig. 5).

IV. CONCLUSIONS

Diphenylpolyenes with $n=3, 4, 5, 6,$ and 7 exhibit dual fluorescence from the S_1 (2^1A_g) and S_2 (1^1B_u) states, but the mechanism for the occurrence of the S_2 fluorescence is different depending on n . S_2 fluorescence occurs as a result of thermal repopulation from the S_1 state due to small S_1 - S_2 energy separations (1000 – 2500 cm^{-1}) for diphenylpolyenes with $n=3$ and 4 . However, S_2 fluorescence occurs as a result of inefficient internal conversion from S_2 to S_1 presumably due to large S_1 - S_2 energy separations (2500 – 5500 cm^{-1}) for diphenylpolyenes with $n=5, 6,$ and 7 . With DP5 whose S_1 - S_2 energy separation ranges from 2000 to 3500 cm^{-1} , both mechanisms were observed for the occurrence of S_2 fluorescence. The series of diphenylpolyenes can be regarded as a rare example showing anti-Kasha emission based on two different mechanisms. Emission property of diphenylpolyenes is suggestive for considering the general rule for the occurrence of anti-Kasha emission.

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