Higher Triplet Excited States of Oligo(*p*-phenylenevinylene)s

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Properties of the higher excited triplet states (T_n) of oligo(*p*-phenylenevinylene)s (OPV*n*, *n* denotes the number of phenyl rings, *n* = 3, 4) were investigated with use of the ns−ps and ns−ns two-color two-laser flash photolysis techniques. The lowest triplet excited states of OPV*n* were generated through the triplet energy transfer (ENT) process by the first 355-nm laser irradiation to the triplet sensitizer. With the delay time of 4 μs after the first laser irradiation, OPV*n*(T_1) was selectively excited with the second 532-nm laser. Bleaching of the absorption of OPV*n*(T_1) was observed during the second ps laser irradiation, indicating the generation of OPV*n*(T_n). The bleaching completely recovered at a few tens of picoseconds after the second picosecond laser irradiation, because of the internal conversion from OPV*n*(T_n) to OPV*n*(T_1). The lifetimes of T_n were estimated to be 35 and 30 ps for OPV3 and OPV4, respectively. In the presence of the triplet energy acceptor (Q), the quenching and recovery of the T_1-absorption bands of OPV*n* were observed because of ENT from OPV*n*(T_n) to Q and Q(T_1) to OPV*n*, respectively. On the basis of the ENT from OPV*n*(T_n) to a series of Q, the T_2−T_1 energy gaps of OPV3 and OPV4 were estimated to be 1.3 and 1.1 eV, respectively.

Introduction

Oligo- and poly(*p*-phenylenevinylene)s have been widely studied both experimentally[1,2,3a] and theoretically[3] because of their applicability to light emitting diodes, field effect transistors, and other devices.[4] Furthermore, oligo(*p*-phenylenevinylene)s are an important electron donor[1a,b,c] and a molecular wire[1d,e] in the photoinduced charge separation systems. Photophysical properties of oligo(*p*-phenylenevinylene)s have been investigated intensively. For example, Janssen et al. have reported the systematic study of the ground and lowest excited state properties of oligo(*p*-phenylenevinylene)s.[2a] Although the lowest excited-state properties are well established, little has been known about the higher excited states.

In general, excitation of organic molecules to the higher triplet excited states (T_n) induces photoionization, energy transfer (ENT), electron transfer, bond dissociation, and isomerization even when these processes are energetically impossible for the S_1 and T_1 states.[5,6a] From the kinetic analysis of the bimolecular ENT process, the lifetimes of the T_n states have been estimated indirectly for several aromatic compounds.[5] Recently, photo-induced processes of the T_n states have been investigated by direct methods with use of short pulse lasers. Hayes et al. have reported the intramolecular ENT from the T_n state of perylene-3,4-dicarboximide to Zn porphyrin in the dyad systems.[6b] We have also reported the properties and reactivities of the olig-othiophenes(T_n) using the ns−ps two-color two-laser flash photolysis method.[6a]

In this paper, we investigated the properties of the T_n states of oligo(*p*-phenylenevinylene)s with 2,5-hexyloxy substituents (OPV*n*, *n* denotes the number of phenyl rings, *n* = 3, 4) (Figure 1) because T_1 and T_n states are selectively generated by the 355- and 532-nm laser excitations, respectively. The lifetimes

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n = 2 (OPV3), 3 (OPV4)
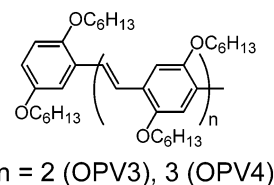
Figure 1. Structures of OPV*n*.

of OPV*n*(T_n) were evaluated directly from the transient absorption changes obtained during the ns−ps two-color two-laser flash photolysis. The T_n energy levels were estimated on the basis of the ENT from OPV*n*(T_n) to a series of energy acceptors. This is the first example of the estimation of T_n energy levels unequivocally by the ENT process.

Experimental Section

Materials. OPV*n* (*n* = 3, 4) were synthesized by the Wittig−Horner coupling reaction.[1a] From ^{1}H NMR, trans-form structures were confirmed for both OPV3 and OPV4. Benzophenone (BP) was purchased from Nacalai Tesque and recrystallized from ethanol. Dibenzoanthracene (Aldrich, 98%) and benzo[*b*]-thiophene (Tokyo Kasei, >97%) were used after recrystallization from toluene and ethanol, respectively. 1,3-Cyclohexadiene was purchased from Aldrich and distilled before use. Anthracene (Aldrich, zone refined, >99%), 1-methylnaphthalene (Tokyo Kasei, >96%), and 3,3′-dimethylbiphenyl (Aldrich, 99%) were used without further purification. Benzene was purchased from Nacalai Tesque (Spectral grade) and used as a solvent without further purification.

Sample solutions were freshly prepared in a quarts cell (optical path length: 0.2 or 0.5 cm) and deoxygenated by bubbling with argon gas for 30 min before irradiation. All experiments were carried out at room temperature.

Apparatus. The ns−ps two-color two-laser flash photolysis was carried out with use of a third harmonic generation (THG,

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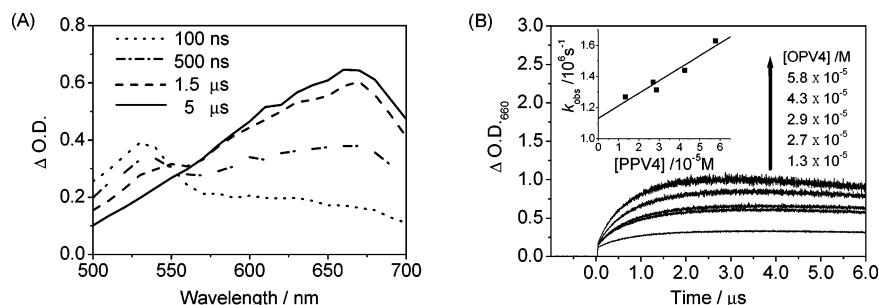
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Figure 2. (A) Transient absorption spectra of OPV4 (2.9×10^{-5} M) in the presence of BP (1.0×10^{-2} M) in benzene at 100 ns, 500 ns, 1.5 μs, and 5 μs during a Nd:YAG (355 nm) laser flash photolysis. (B) Kinetic traces of ΔOD at 660 nm. Inset: pseudo-first-order plot.

355 nm) of a nanosecond Nd:YAG laser (Quantel, Brilliant, fwhm 5 ns) and second harmonic generation (SHG, 532 nm) of a picosecond Nd:YAG laser (Continuum, RGA69−10LD, fwhm 30 ps) as the first and second lasers, respectively. The first laser was irradiated at 4 μs before the second laser with use of a delay circuit (Stanford Research Systems, DG-535). A white continuum pulse generated by focusing the fundamental of the picosecond Nd:YAG laser on a D_2O/H_2O (1:1 volume) cell was used as the monitoring light and detected with a MOS linear imaging head (Hamamatsu Photonics, M2493-40) equipped with a polychromator (Hamamatsu Photonics, C5094). The ns−ns two-color two-laser flash photolysis was carried out with THG (355 nm) of a Nd:YAG laser (Quantel, Brilliant, fwhm 5 ns) and SHG (532 nm) of a Nd:YAG laser (Continuum, Surelite, fwhm 5 ns) as the first and second lasers, respectively. The monitoring light from a pulsed Xe lamp (Osram, XBO-450, 450 W) was detected with a Si-avalanche photodiode (Hamamatsu Photonics, S5343) equipped with a monochromator (Nikon, G250).

Results and Discussion

OPV*n* in the T_1 States. It has been reported that the intersystem crossing yields of alkoxy-substituted oligo(*p*-phenylenevinylene)s are quite small. For example, the inter-system crossing yield of 1,4-bis(octyloxy)-2,5-bis[(1*E*)-2-(4-(1*E*)-2-phenylethenyl)phenylethenyl]benzene has been reported to be 0.04.[2d] Therefore, in the present paper, OPV*n*(T_1) was generated by the triplet sensitization with BP as the sensitizer. Figure 2 shows transient absorption spectra and kinetic traces for the sensitization of OPV4(T_1) with BP during the 355-nm laser flash photolysis. Generation of OPV4(T_1) at 660 nm with decay of BP(T_1) clearly indicates the sensitization. From a pseudo-first-order plot of the observed rate constant (k_{obs}) on the concentration of OPV4 (inset of Figure 2B), the ENT rate constant from BP(T_1) to OPV4(S_0) (k_{ENT}) was estimated to be 8.1×10^9 M^{-1} s^{-1}. Furthermore, the extinction coefficient of OPV4(T_1) (ϵ_{T_1}) was estimated to be 1.3×10^5 M^{-1} cm^{-1} at 660 nm, employing that of BP(T_1) as a reference.[7] As for OPV3, the T_1 ENT rate constant and ϵ_{T_1} value were estimated to be 4.8×10^9 M^{-1} s^{-1} and 9.8×10^4 M^{-1} cm^{-1} at 540 nm, respectively. From the pulse radiolysis, the ϵ_{T_1} values of *tert*-butyl or alkoxy substituted oligo(*p*-phenylenevinylene)s(T_1) (*n* = 3, 5, 7, and 9) in benzene have been reported to be in the range of 1.4 to 1.9×10^5 M^{-1} cm^{-1},[2c,d] which are similar to the present experimental results. Furthermore, the intersystem crossing yields (ϕ_{ISC}) were estimated to be 3.6×10^{-3} and 7.5×10^{-4} for OPV3 and OPV4, respectively, from the actinometry with BP(T_1) as a standard. Therefore, introduction of the alkoxy substitutes efficiently decreases the intersystem crossing quantum yields of oligo(*p*-phenylenevinylene)s.

TABLE 1: Energy Transfer Rate Constants of the Sensitization of OPV*n*

| | | $k_{ENT}/10^9$ M^{-1}s^{-1} | |
sensitizer	E_{T_1}/eV[7]	OPV3	OPV4
benzophenone	3.0	4.8	8.1
anthracene	1.8	7.7	10
9,10-dibromoanthracene	1.7	4.0	7.0
zinc tetraphenylporphyrin	1.6	0.47[a,b]	1.0
tetraphenylporphyrin	1.4	1.5[a,b]	a

[a] OPV*n* was not sensitized. [b] The ENT rate from OPV3 to sensitizer.

SCHEME 1: Energy Diagram of ns−ps Two-Color Two-Laser Flash Photolysis
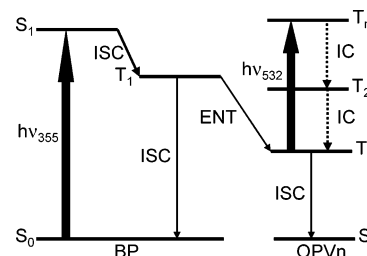
To estimate the T_1 energies of OPV*n* (E_{T_1}), the triplet sensitizations were examined with a series of energy donors (Table 1). In the cases of BP, anthracene, and dibromoan-thracene, OPV3 was sensitized at the rate close to the diffusion-controlled rate. On the other hand, zinc tetraphenylporphyrin (ZnTPP) and tetraphenylporphyrin (H$_2$TPP) were sensitized by OPV3(T_1), indicating that E_{T_1} of OPV3(T_1) is slightly higher than E_{T_1} of ZnTPP(T_1). As for OPV4, the ENT from the ZnTPP-(T_1) was observed, while the ENT from H$_2$TPP(T_1) did not occur, indicating that E_{T_1} of OPV4(T_1) is lower than E_{T_1} of ZnTPP(T_1). The energy levels of OPV3(T_1) and OPV4(T_1) were estimated to be 1.6 ± 0.1 and 1.5 ± 0.1 eV, respectively. The properties of OPV*n*(T_1) were summarized in Table 2.

OPV*n* in the T_n States. OPV*n*(T_1) generated by the triplet sensitization with BP was excited by the picosecond laser (532 nm, fwhm 30 ps, 10 mJ pulse^{-1}) at 4 μs after the first laser excitation, which ensures the complete deactivation of BP(T_1) according to Scheme 1. Actually, at 50 ps before the second laser irradiation, generation of OPV3(T_1) was confirmed (Figure 3A). The absorption band of OPV3(T_1) was bleached at 40 ps after the second laser irradiation, and recovered completely at 300 ps after the second laser excitation. This indicates the generation of OPV3(T_n) immediately after the second excitation and quantitative deactivation to OPV3(T_1) through the internal conversion. An absorption band attributable to OPV3(T_n) was not observed, probably because of the small extinction coef-ficient of the T_n state. Absence of new absorption peaks of T_n was also reported for trimer of thiophene, although tetramer

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TABLE 2: T$_1$ and T$_n$ Properties of OPVn

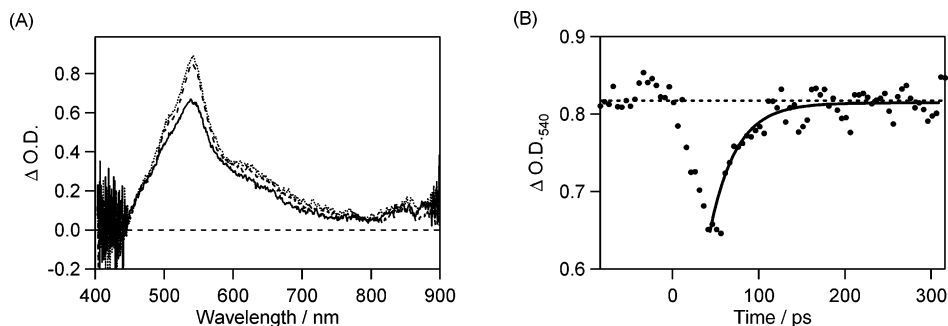| OPVn	E_{T_1}/eV	$\tau_{T_1}{}^a$/ 10^{-6} s	ϵ_{T_1}/10^4 M^{-1} cm^{-1}	ϕ_{ISC}/10^{-3}	E_{T_n}/eV	$\Delta E_{T_n-T_1}$/eV	τ_{T_n}/10^{-12} s
OPV3	1.6 ± 0.1	20	9.8	3.6	2.9 ± 0.1	1.3 ± 0.2	35
OPV4	1.5 ± 0.1	16	13	0.75	2.6 ± 0.1	1.1 ± 0.2	30

^{a} Lifetimes of OPVn(T$_1$)

Figure 3. (A) Transient absorption spectra of OPV3 in benzene observed at 50 ps before (dotted line) and 40 (solid line) and 300 ps (broken line) after the second laser irradiation during ns−ps two-color two-laser flash photolysis employing a nanosecond Nd:YAG laser (355 nm, fwhm 5 ns, 10 mJ pulse^{-1}) and a picosecond Nd:YAG laser (532 nm, fwhm 30 ps, 10 mJ pulse^{-1}). (B) Kinetic trace of ΔOD at 540 nm. The solid line is a fitted line.
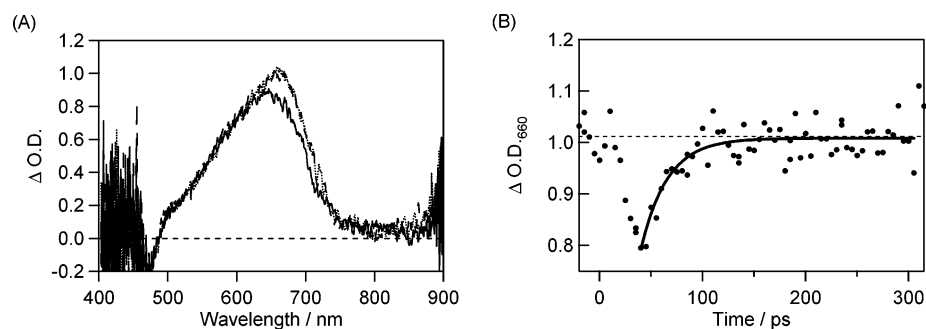

Figure 4. (A) Transient absorption spectra of OPV4 in benzene observed at 20 ps before (dotted line) and 40 (solid line) and 300 ps (broken line) after the second laser irradiation during ns−ps two-color two-laser flash photolysis employing a nanosecond Nd:YAG laser (355 nm, fwhm 5 ns, 10 mJ pulse^{-1}) and a picosecond Nd:YAG laser (532 nm, fwhm 30 ps, 10 mJ pulse^{-1}). (B) Kinetic trace of ΔOD at 660 nm. The solid line is a fitted line.

and pentamer of thiophene showed absorption bands assigned to the T$_n$ states.[6a] From the deconvolution fitting of single-exponential function to the kinetic trace of ΔOD at 540 nm, the rate constant of the recovery of the T$_1$ state (k_{IC}) was estimated to be $(2.9 \pm 0.2) \times 10^{10}$ s^{-1}, which corresponds to 35 ps of the lifetime of OPV3(T$_n$) (τ_{T_n}).

In the case of OPV4, bleaching and complete recovery of the T$_1$ absorption were also confirmed (Figure 4A). It should be noted that the absorption of OPV4(T$_1$) did not decrease homogeneously. The absorption in the region of 480−630 nm did not decrease, while a shoulder appeared around 680 nm. These results indicate that the formation of the absorption band of OPV4(T$_n$) is overlapping with bleaching of OPV4(T$_1$). The k_{IC} value of OPV4(T$_n$) was $(3.3 \pm 0.3) \times 10^{10}$ s^{-1}, which corresponds to 30 ps of τ_{T_n} (Figure 4B).

When the fluence of the second laser increased, the absorption bands of T$_1$ were not recovered completely. For example, the recovery yields were 82% and 75% of the initial bleaching of OPV3(T$_1$) and OPV4(T$_1$), respectively, when the laser fluence was 25 mJ pulse^{-1}. It should be noted that the amount of incomplete recovery increased in a nonlinear manner with the laser fluence. Therefore, the incomplete recovery can be attributed to nonlinear process(es) such as the two-photon process from the T$_1$ state. It was revealed that this nonlinear process induced the decomposition of OPVn. Therefore, all photophysical and chemical properties of OPVn(T$_n$) were estimated under the condition where the nonlinear process can be ignored.

The internal conversion rates depend on the T$_2$−T$_1$ energy gap.[8] To investigate the relation between k_{IC} and the energy gap, the T$_2$ energies were estimated in the next section.

Quenching of OPVn(T$_n$). For some aromatic hydrocarbons, ENT processes from T$_n$ states to quenchers have been reported.[5] The ENT was observed as the bleaching of the T$_1$ absorption band during ns−ns two-color two-laser flash photolysis. In principle, ENT from the T$_n$ state proceeds only when the T$_1$ energy of the energy acceptor is lower than the triplet energy of the T$_n$ state of the donor. Therefore, the energy level of the T$_n$ state can be estimated from the ENT by changing E_{T1} of the energy acceptors. In the present study, 1,3-cyclohexadiene (E_{T1} = 2.3 eV), 1-methylnaphthalene (2.6 eV), 3,3′-dimethyl-biphenyl (2.8 eV), and benzo[*b*]thiophene (3.0 eV) were used as the energy acceptor of OPVn(T$_n$).[7]

Figure 5 shows the kinetic traces of OPV3(T$_n$) in the presence of 1-methylnaphthalene as the energy acceptor during the ns−ns two-color two-laser flash photolysis as a representative. The bleaching of the absorption band was observed with the second laser flash, indicating the ENT from OPV3(T$_n$) to 1-methyl-naphthalene generating 1-methylnaphthalene(T$_1$). It should be pointed out that the bleaching was recovered at a few micro-seconds after the second laser flash, indicating the regeneration of OPV3(T$_1$) by the ENT from 1-methylnaphthalene(T$_1$) to OPV3 (Scheme 2). Similar ENT processes were observed when 1,3-cyclohexadiene and 3,3′-dimethylbiphenyl are used as the acceptor. On the other hand, ENT with benzo[*b*]thiophene was not confirmed, indicating that the OPV3(T$_n$) lies between 2.8
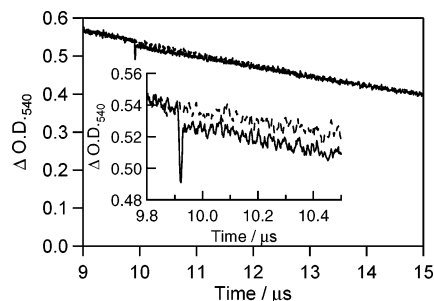
Figure 5. Kinetic traces of ΔOD at 540 nm during the ns–ns two-color two-laser flash photolysis of OPV3 in the presence of 1-methylnaphthalene (1.0 M). The second laser was irradiated at 9.9 μs after the first laser. Broken and solid lines show single laser and two-laser photolysis, respectively. Inset: The enlargement of the initial part. The spike signal at the second laser flash is due to laser scattering.

SCHEME 2: Energy Diagram of the ENT Processes from OPVn(T$_n$)
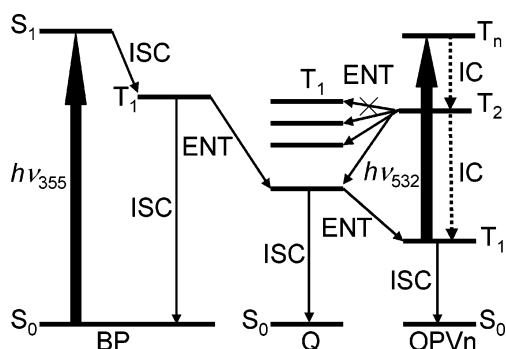
and 3.0 eV, i.e., 2.9 $\pm$ 0.1 eV. For OPV4(T$_n$), the T$_n$ energy (E_{T_n}) was estimated to be 2.6 $\pm$ 0.1 eV (Table 2). It should be noted that these are the first example of the estimation of the T$_n$ energy levels unequivocally by the ENT process.

Energetic Considerations of OPVn(T$_n$). From the ENT with a series of energy acceptors, the T$_n$ and T$_1$ energy levels of OPVn were estimated. Therefore, the energy gaps between the T$_n$ and T$_1$ states ($\Delta E_{T_n-T_1}$) are 1.3 $\pm$ 0.2 and 1.1 $\pm$ 0.2 eV for OPV3 and OPV4, respectively. It is known that τ_{T_n} becomes longer with increasing the T$_n$–T$_1$ energy gap.[8] For example, the lifetimes of naphthalene, anthracene, and chrysene in the T$_2$ states were reported to be 4.5, 11, and 60 ps, while corresponding T$_2$–T$_1$ energy gaps are 1.17, 1.39, and 1.75 eV, respectively.[5,9] In the case of OPVn(T$_n$), a longer τ_{T_n} with a larger T$_n$–T$_1$ energy gap was confirmed. It should be pointed out that the absorption maxima of the T$_1$ states of OPV3 (540 nm) and OPV4 (660 nm) correspond to larger energies than the energy gaps corresponding to the present internal conversion. Therefore, these results indicate that the second laser excites the T$_1$ state to the T$_{n'}$ states ($n' > n$) followed by the rapid internal conversion to the T$_n$ states which have the τ_{T_n} values of a few tens of picoseconds.

The triplet manifold of OPVn(T$_n$) is not clear. In the cases of the trimer and tetramer of oligothiophenes(T$_n$), which have the nondegenerated electronic structures similar to OPVn(T$_n$), internal conversion of oligothiophenes(T$_n$) occurs very rapidly to give oligothiophenes(T$_2$) with the longest τ_{T_n} among oligothiophenes(T$_n$). The T$_2$–T$_1$ gaps were estimated to be 1.5–1.4 eV,[10] and the corresponding τ_{T_n} values of trimer and tetramer of oligothiophenes(T$_2$) are 38 ps.[6a] The estimated τ_{T_n} values of OPVn(T$_n$) and corresponding energy gaps between the T$_1$ and T$_n$ states are very close to those of oligothiophenes(T$_2$). Therefore, OPVn(T$_n$) with the longest lifetime possibly can be assigned to OPVn(T$_2$).

Conclusions

In the present study, the properties of the T$_n$ states of OPVn were investigated with use of the two-color two-laser flash photolysis method. The T$_n$ states of OPVn were completely deactivated to the T$_1$ states in benzene. The τ_{T_n} values of OPV3-(T$_n$) and OPV4(T$_n$) were directly estimated to be 35 and 30 ps, respectively, using a picosecond laser flash. Although those τ_{T_n} values are in the order of picoseconds, they are long enough for the intramolecular ENT and electron transfer as evidenced by the intermolecular ENT reactions in the present study. Furthermore, the ENT processes revealed the energy levels of the T$_1$ and T$_n$ states of OPVn. These results are beneficial for the prediction of the photoinduced processes of the T$_n$ states. The T$_n$ states are assigned to the T$_2$ states based on the τ_{T_n} values of the T$_n$ states and the T$_n$–T$_1$ energy gaps.

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