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Dendron-Containing Tetraphenylethylene Compounds: Dependence of Fluorescence and Photocyclization Reactivity on the Dendron Generation

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Abstract: The synthesis and characterization of four dendron-containing tetraphenylethylenes (TPEs), $\mathbf{1}_1$–$\mathbf{1}_4$, were synthesized, along with a TPE compound that contained four OCH_2Ph groups (referred to as $\mathbf{1}_0$) for comparison. Photophysical studies revealed that the TPE core became emissive after linking dendrons onto its periphery. Moreover, the fluorescence intensity was significantly enhanced when high-generation dendrons were linked onto the TPE core; the fluorescence intensity increased in the following order: $\mathbf{1}_1 < \mathbf{1}_2 < \mathbf{1}_3 < \mathbf{1}_4$. This phenomenon was tentatively attributed to an enhancement in the energy barrier for internal rotation and torsion of the TPE core to which four dendrons were connected. In addition, the photocyclization of the TPE core into the respective 9,10-diphenylphenanthrene was facilitated when high-generation dendrons were linked to the TPE core. Again, the photocycliztion reactivity increased in the following order: $\mathbf{1}_1 < \mathbf{1}_2 < \mathbf{1}_3 < \mathbf{1}_4$. We found that the fluorescence and photocyclization reactivity of TPE could be modulated by covalent interactions with dendrons, and such modulation was strongly dependent on the dendron-generation.

Keywords: cyclization · dendrons · fluorescence · photochemistry · tetraphenylethylene

Introduction

Tetraphenylethylene (TPE) and its derivatives have been heavily investigated, both experimentally and theoretically.[1] It is well-known that structural relaxations, induced mainly by phenyl and phenylvinyl rotational/torsional motions,[2] are effective upon photoexcitation; such structural relaxations deactivate the excited states of TPE molecules, and therefore TPE compounds are almost non-emissive in solution. Tang and co-workers, among others, have reported that the fluorescence of TPE compounds becomes significantly enhanced following aggregation.[2a–c] In fact, Li and co-workers have reported the fluorescence enhancement of other types of organic molecules (e.g. styryl-type molecules).[2d,e] Based on fluorescence spectroscopy studies under various conditions, it is assumed that aggregation largely inhibits the internal rotation and torsion that are responsible for non-radiation pathways. In fact, TPEs are strongly emissive in the solid state and have been used as light-emitting materials for OLEDs (organic light-emitting diodes).[3] Recently, a number of chemo-/biosensors have been reported that take advantage of such abnormal fluorescence properties of TPE compounds.[4,5]

Apart from aggregation, in principle it is also possible to inhibit the internal rotation and torsion by modifying the TPE framework or by linking appropriate groups to the TPE core. For instance, Fox and co-workers[2b] reported that the TPE framework became more rigid and the torsion of the phenyl ring was inhibited when the phenyl rings were connected through shorter hydrocarbon tethers within the cyclic tetraphenylethylenes; as a result, the fluorescence of these cyclic tetraphenylethylenes was enhanced notably. Vyas and Rathore[6a] and Wang and co-workers[6b] separately described the restriction of internal rotation and torsion for TPEs by increasing the steric hindrance within tetrakis(pentaphenylphenyl)ethylene and TPE oligomers. Moreover, the inhibition of internal rotation and torsion by encapsulation is also characteristic of green fluorescent protein.[7]

Dendrimers, as regularly branched, 3D architectures, have received significant attentions over the past few decades.[8,9] Various functional groups can be positioned either at the cores of the dendrimers, in the branching units, and/or on the exterior surfaces. Encapsulation of various fluorophores with dendrons has long been reported. It is anticipated that dendron-capped fluorophores would become more-emissive because, at least, the collisional quenching of their exited states can be suppressed to some extent, in particular upon incremental increase of the generation number of the dendron. However, fluorescence enhancement has only been observed for a few encapsulated fluorophores with den-

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drons.[10] Interesting dendrimer effects on fluorescence behavior have been demonstrated in several systems.[11]

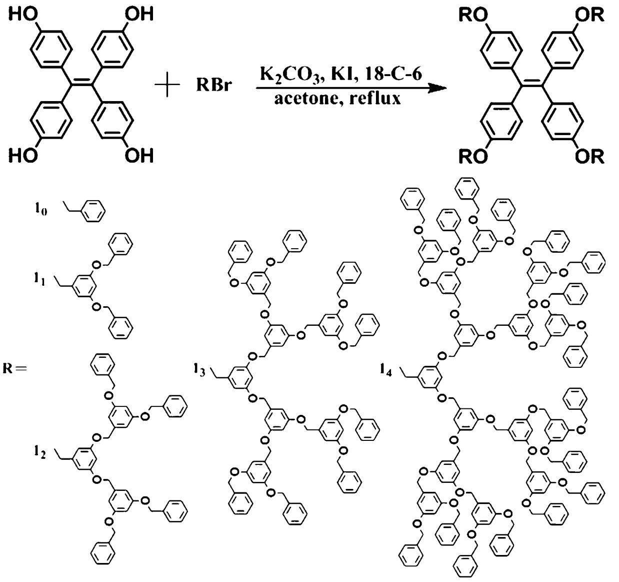
Herein, we report TPE compounds $\mathbf{1}_1$–$\mathbf{1}_4$ (see Scheme 1), which were capped with dendrons of different generation numbers that were constructed by using benzyl ether. For comparison, a TPE compound with four OCH_2Ph groups ($\mathbf{1}_0$) is also reported. We aimed to investigate whether it was possible to inhibit the internal torsion and rotation of the TPE core, and thus activate its excited state, by linking four dendrons of different generations onto the periphery of TPE (Scheme 1). Our molecular design was based on the following considerations: 1) compared to the TPE core, benzyl-ether-based dendrons of high generation number are bulky, and thus the energy barriers for internal structural torsion and rotation for dendron-containing TPEs are expected to be higher than those for TPEs without substituents; 2) high-generation dendrons may adopt hemispherical or even spherical 3D structures, which may "clip" the phenyl rings of the TPE core to suppress the internal structural torsion and rotation; 3) encapsulation of the TPE core by dendrons may avoid the collision of solvent molecules. The fluorescence of these dendron-containing TPE compounds is enhanced upon incremental increase of the dendron generation number (see below). Moreover, the photocyclization reactivity of the TPE core was dependent on the dendron generation number. These results revealed that the excited-state behaviors of TPE could be modulated by linking dendrons onto its periphery.

Results and Discussion

Synthesis: The synthesis of compounds $\mathbf{1}_0$, $\mathbf{1}_1$, $\mathbf{1}_2$, $\mathbf{1}_3$, and $\mathbf{1}_4$ started from tetrakis(4-hydroxyphenyl)ethylene and the corresponding dendritic benzyl bromides, both of which were prepared according to literature procedures.[12] The reactions between tetrakis(4-hydroxyphenyl)ethylene and the corresponding dendritic benzyl bromides were carried out in the presence of K_2CO_3, KI, and [18]crown-6 in acetone (Scheme 1). The dendron-containing TPE compounds were obtained after chromatographic separation. Their chemical structures and purities were confirmed by NMR spectroscopy, MS, and elemental analysis.

Absorption and fluorescence spectroscopy: The Supporting Information, Figure S1 shows the absorption spectra of solutions of compounds $\mathbf{1}_0$, $\mathbf{1}_1$, $\mathbf{1}_2$, $\mathbf{1}_3$, and $\mathbf{1}_4$ in THF. All of these TPE compounds exhibited absorption peaks at 238, 276, and 330 nm. Compared to compound $\mathbf{1}_0$, the different absorption intensities at 238 and 276 nm were due to the presence of different benzene rings in the corresponding dendrons of compounds $\mathbf{1}_1$–$\mathbf{1}_4$. Thus, the electronic coupling between the TPE core and the respective dendron within compounds $\mathbf{1}_1$–$\mathbf{1}_4$ can be neglected.

Figure 1 shows the fluorescence spectra of solutions of compounds $\mathbf{1}_0$, $\mathbf{1}_1$, $\mathbf{1}_2$, $\mathbf{1}_3$, and $\mathbf{1}_4$ in THF. Compound $\mathbf{1}_0$ was almost non-emissive, owing to the internal rotation and torsion expected for TPE compounds. Fluorescence began to emerge for compounds $\mathbf{1}_1$ and $\mathbf{1}_2$, but the intensities were rather weak. Interestingly, compounds $\mathbf{1}_3$ and $\mathbf{1}_4$ exhibited relatively strong fluorescence, with $\lambda_{max} = 487$ nm. Their fluorescence intensities increased in the order: $\mathbf{1}_0 < \mathbf{1}_1 < \mathbf{1}_2 < \mathbf{1}_3 < \mathbf{1}_4$. As shown in Figure 1 inset, the fluorescence of compounds $\mathbf{1}_3$ and $\mathbf{1}_4$ were easily detectable by the naked-eye, whilst compounds $\mathbf{1}_1$ and $\mathbf{1}_2$ were almost non-emissive under UV-light irradiation. The corresponding fluorescence quantum yields (Table 1) increased notably upon incremental increase of the generation number for these dendron-containing TPE compounds. For instance, the fluorescence quantum yield of compound $\mathbf{1}_4$ was 22 times higher than that of compound $\mathbf{1}_1$ in THF. The fluorescence quantum yields of compounds $\mathbf{1}_1$–$\mathbf{1}_4$ were slightly dependent on solvent properties, as shown in Table 1; for instance, that of compound $\mathbf{1}_4$



Scheme 1. Chemical structures and synthesis of compounds $\mathbf{1}_0$, $\mathbf{1}_1$, $\mathbf{1}_2$, $\mathbf{1}_3$, and $\mathbf{1}_4$. 18-C-6 = [18]crown-6.

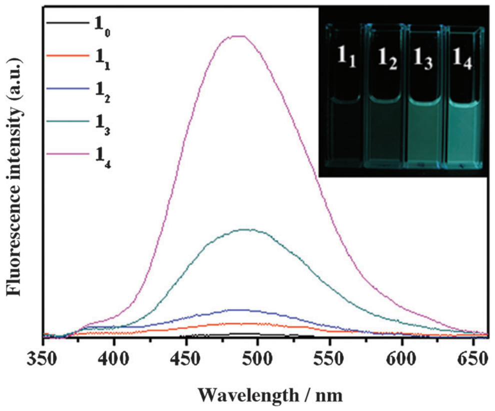


Figure 1. Emission spectra ($\lambda_{ex} = 340$ nm) of compounds $\mathbf{1}_0$, $\mathbf{1}_1$, $\mathbf{1}_2$, $\mathbf{1}_3$, and $\mathbf{1}_4$ at RT. The concentration of each compound was 1.0×10^{-5} mol L^{-1} in THF. Inset: photographs of solutions of compounds $\mathbf{1}_1$–$\mathbf{1}_4$ in THF taken under illumination from a UV lamp.

Table 1. Photophysical parameters of compounds $\mathbf{1}_1$–$\mathbf{1}_4$.

	$\mathbf{1}_1$	$\mathbf{1}_2$	$\mathbf{1}_3$	$\mathbf{1}_4$
λ_{abs} [nm][b]	330	330	332	328
λ_{em} [nm][b]	487	487	487	487
τ [ns][b]	0.087	0.085	0.222 (86.14 %) 2.090 (13.86 %)	0.654 (62.79 %) 2.929 (37.21 %)
Φ_f[a,b]	0.004	0.011	0.033	0.093
Φ_f[a,c]	0.007	0.018	0.069	0.195
Φ_f[a,d]	0.011	0.029	0.071	0.193

[a] The fluorescence quantum yield (Φ_f) was measured with 9,10-diphenylanthracene (DPA) in EtOH ($\Phi_f = 90\,\%$) as the standard. The absorbance of each solution at 330 nm (the excitation wavelength) was adjusted to be less than 0.05. [b] In THF. [c] In toluene. [d] In DMSO.

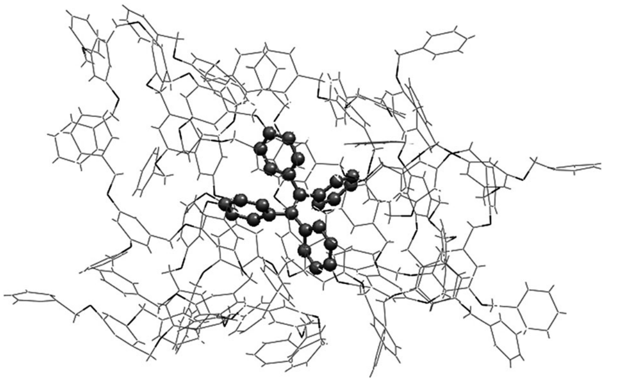


Figure 2. Stable conformation of compound $\mathbf{1}_3$ obtained by molecular dynamic (MD) simulations.

reached 0.195 in toluene. On the basis of the fluorescence-decay data, the fluorescence lifetimes of compounds $\mathbf{1}_1$–$\mathbf{1}_4$ were evaluated and shown in Table 1. Compounds $\mathbf{1}_1$ and $\mathbf{1}_2$ exhibited single lifetimes of 0.087 and 0.085 ns, respectively, but two fluorescence lifetimes were obtained for compounds $\mathbf{1}_3$ and $\mathbf{1}_4$.[13] Importantly, the fluorescence lifetimes of compounds $\mathbf{1}_3$ and $\mathbf{1}_4$ were much longer than those of compounds $\mathbf{1}_1$ and $\mathbf{1}_2$. These photophysical data for these dendron-containing TPE compounds suggested that the fluorescence of the TPE core could be enhanced by linking dendrons of high generation onto its periphery.

The influence of dendrons on the fluorescence properties of the TPE core may be attributed to the following points: 1) encapsulation of TPE core by the dendrons may shield the core from the solvent, and thus collisional quenching may be eliminated; 2) the presence of dendrons may make the TPE core more rigid and enhance the barrier for internal rotation and torsion, thereby inhibiting these non-radiative pathways. The fluorescence spectra of compounds $\mathbf{1}_1$–$\mathbf{1}_4$ were also recorded in other solvents, and the fluorescence quantum yields varied accordingly (Table 1). For instance, the Φ_f value of compound $\mathbf{1}_4$ increased from 0.093 in THF to 0.195 and 0.193 in toluene and DMSO, respectively. Such solvent-dependence implied that the fluorescence enhancement of compounds $\mathbf{1}_1$–$\mathbf{1}_4$ was not solely caused by inhibition of the collisional quenching by shielding the TPE core with four dendrons. Therefore, the inhibition of internal rotation and torsion owing to the presence of the dendrons presumably also contributed to the fluorescence enhancement for compounds $\mathbf{1}_1$–$\mathbf{1}_4$. In fact, the structures of compounds $\mathbf{1}_1$–$\mathbf{1}_4$ were investigated with molecular-dynamics (MD) simulations (see the Supporting Information). As an example, Figure 2 shows the simulated structure of compound $\mathbf{1}_3$. It was clear that the TPE core was tightly surrounded by the third-generation dendrons. Thus, we expected that the internal rotation and torsion of the TPE core would be significantly restricted. According to previous reports, the TPE core would be expected to be even-more-tightly encapsulated by dendrons of higher generation (e.g. $\mathbf{1}_4$), and thus the energy barriers for internal rotation and torsion would be higher, thereby leading to the inhibition of these internal motions and thus to fluorescence enhancement of the TPE core. Accordingly, it was understandable that the fluorescence of these TPE compounds increased upon increasing the dendron generation number in the order: $\mathbf{1}_1 < \mathbf{1}_2 < \mathbf{1}_3 < \mathbf{1}_4$. Variation of the fluorescence quantum yields of these TPE compounds in different solvents may be due to the fact that the dendrons adopted different conformations and, as a result, the TPE core was differently encapsulated.

The fluorescence of compound $\mathbf{1}_4$ was enhanced further through the addition of water to its solution in THF (Figure 3). The fluorescence intensity of compound $\mathbf{1}_4$ increased gradually with increasing water content. This result was different from the parent TPE compound and its derivatives, for which the fluorescence intensities increased only slightly when the water content was below a critical amount, but then increased abruptly when the water content was above the critical amount.[5a–b] For instance, the fluorescence intensity of compound $\mathbf{1}_4$ at 444 nm was enhanced by 0.6, 3.6, and 7.3 times when the volume ratio of water in the solution reached 20 %, 60 %, and 90 %, respectively. However, when the water volume ratio increased to 95 %, the fluorescence intensity was slightly reduced. This result was probably due to the formation of aggregates with different morphologies within which the intermolecular packing may be changed.[6b, 14] Moreover, the fluorescence maximum was

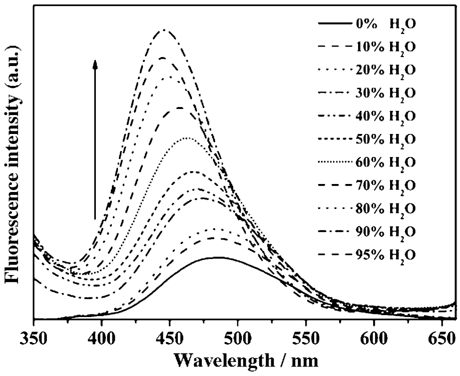


Figure 3. Fluorescence spectra of compound $\mathbf{1}_4$ (1.0×10^{-5} mol L^{-1}; $\lambda_{ex} =$ 340 nm) in a THF/water mixture with various amounts of water.

blue-shifted along with the enhancement in fluorescence intensity. Similar fluorescence enhancement and blue-shifts were detected for compounds $\mathbf{1_1}$–$\mathbf{1_3}$ (see the Supporting Information, Figure S7). For compound $\mathbf{1_0}$, the fluorescence intensity was only enhanced when the water content was higher than 40%.

According to previous reports, compounds $\mathbf{1_0}$, $\mathbf{1_1}$, $\mathbf{1_2}$, $\mathbf{1_3}$, and $\mathbf{1_4}$ were not water-soluble and thus the addition of water to their solutions in THF would lead to aggregation. In fact, solutions of compounds $\mathbf{1_1}$–$\mathbf{1_4}$ became opaque when the water content was higher than 30%. After the addition of water, the solutions of compounds $\mathbf{1_1}$–$\mathbf{1_4}$ were subjected to DLS (dynamic light scattering) studies. For instance, particles with sizes of around 212.5 nm were detected for the solution of compound $\mathbf{1_4}$ in THF with 95% water content (see the Supporting Information, Figure S8). Previous studies[4,5] indicated that the aggregation of TPE compounds could induce fluorescence enhancement, which was typically attributed to the restriction of internal rotation after aggregation. However, for compounds $\mathbf{1_3}$ and $\mathbf{1_4}$, we anticipated that their aggregation would lead to interdendron interactions, which would impose additional barriers to the internal rotation and torsion of the TPE cores. The shifts in the emission maxima may be due to the fact that the TPE core became more twisted because of the interdendron interactions, in particular for high-generation dendrons, and, as a result, the π-conjugation within the TPE core was reduced. However, for compound $\mathbf{1_0}$, the TPE core was not well-shielded by the substituents, and thus the intermolecular interactions of the benzene rings may affect the π-conjugation within the TPE core, thus leading to variation of the emission maximum. More studies on this property are underway.

Photocyclization reactions: The emission color of a solution of compound $\mathbf{1_4}$ in THF gradually transformed from green to blue on standing under ambient conditions for several hours (Figure 4a, inset). In fact, the fluorescence spectrum of compound $\mathbf{1_4}$ varied significantly upon UV-light (350 nm) irradiation: the intensity of the fluorescence at around 487 nm became gradually weaker and a new emission at around 387 nm emerged simultaneously (Figure 4a). The absorption spectrum of compound $\mathbf{1_4}$ also changed (Figure 4b): the absorption at around 330 nm gradually decreased and two weak absorption peaks at around 354 and 372 nm appeared. Appealingly, these new fluorescence and absorption spectra were rather similar to those of 9,10-diphenylphenanthrene and its derivatives,[15,16] which indeed can be generated by the oxidative photocyclization of tetraphenylethylenes.[15] Therefore, these results suggested that the TPE core of compound $\mathbf{1_4}$ could be converted into its corresponding 9,10-diphenylphenanthrene derivative ($\mathbf{2_4}$) upon UV-light irradiation, in the presence of oxygen (Scheme 2).[17] Such a photochemical reaction has long been known, but it typically requires long irradiation times for the transformation to be completed.[15]

Both MS and ^{1}H NMR spectroscopic data were collected to support the above photocyclization reaction of compound $\mathbf{1_4}$. A signal at m/z 13518 was detected for the solution of compound $\mathbf{1_4}$ after UV-light irradiation with exposure to air, which corresponded to the molecular weight of the respective photocyclization product ($\mathbf{2_4}$) plus K^+. Moreover, the ^{1}H NMR signal owing to the protons of the TPE core ($\delta =$ 6.87 ppm) disappeared, and signals at $\delta = 6.77$, 6.94, and 8.17 ppm emerged after UV irradiation for just 11 min (see the Supporting Information, Figure S18). To confirm the assignment for compound $\mathbf{1_4}$ after UV irradiation, the ^{1}H NMR spectrum of compound **1** (tetrakis(p-methoxylphenyl)ethylene) was recorded after UV-light irradiation for different periods of time (see the Supporting Information, Figure S13). The signals attributed to the aromatic protons of compound **1** ($\delta = 6.67$ and 6.83 ppm) disappeared, and

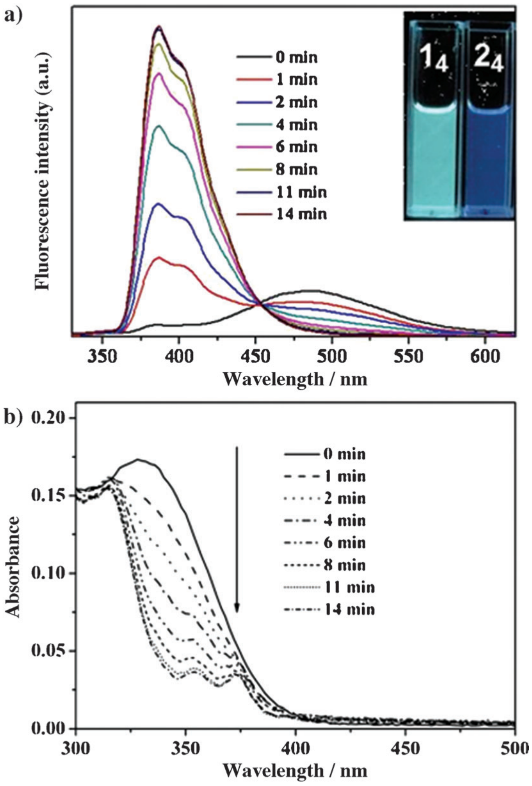
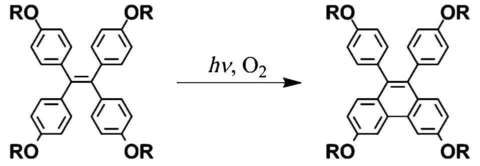


Figure 4. a) Emission spectra and b) absorption spectra of compound $\mathbf{1_4}$ (1.0×10^{-5} mol L^{-1} in THF) after UV-light irradiation (350 nm) for different periods of time. Inset: photographs of solutions of compounds $\mathbf{1_4}$ and $\mathbf{2_4}$ in THF taken under illumination from a UV lamp.



1 R = CH_3
$\mathbf{1_0}$ R = CH_2Ph
$\mathbf{1_1}$–$\mathbf{1_4}$ R = dendron unit

2 R = CH_3
$\mathbf{2_0}$ R = CH_2Ph
$\mathbf{2_1}$–$\mathbf{2_4}$ R = dendron unit

Scheme 2. The photocyclization reactions and chemical structures of the photocyclization products (**2**, $\mathbf{2_0}$, $\mathbf{2_1}$, $\mathbf{2_2}$, $\mathbf{2_3}$, and $\mathbf{2_4}$).

new signals at $\delta = 6.82$, 7.03, 7.18, 7.28, and 8.23 ppm were observed after irradiation for 3 h. The signal assigned to four methoxy groups ($\delta = 3.66$ ppm) split into two signals at $\delta = 3.72$ and 3.99 ppm (see the Supporting Information, Figure S13). In fact, the ^{1}H NMR spectrum of compound **1** after UV-light irradiation was almost identical to that of the known compound **2** (3,6-dimethoxy-9,10-bis(4-methoxyphenyl)-phenanthrene).[15c] Thus, we concluded that compound **1** was converted into compound **2** after UV-light irradiation for a certain period of time. The ^{1}H NMR signal at around $\delta = 8.20$ ppm was used as a characteristic peak to verify the formation of the photocyclization reaction product. As shown in the Supporting Information, Figure S18, new ^{1}H NMR signals at $\delta = 6.77$, 6.94, and 8.17 ppm (in particular) gradually appeared for the solution of compound $\mathbf{1_4}$ after UV-light irradiation. This ^{1}H NMR data[18] provided direct evidence for the transformation of the TPE core of compound $\mathbf{1_4}$ into 9,10-diphenylphenanthrene.

Similar changes in the fluorescence and absorption spectra were observed for compounds $\mathbf{1_0}$, $\mathbf{1_1}$, $\mathbf{1_2}$, and $\mathbf{1_3}$ after UV-light irradiation (see the Supporting Information, Figures S9–S12): 1) the fluorescence intensity at around 487 nm decreased and a new emission at around 387 nm appeared simultaneously, and 2) the absorption at around 330 nm gradually weakened. These changes implied that the TPE core of compound $\mathbf{1_4}$ had undergone photocyclization into 9,10-diphenylphenanthrene. In addition, the ^{1}H NMR spectra of compounds $\mathbf{1_0}$, $\mathbf{1_1}$, $\mathbf{1_2}$, and $\mathbf{1_3}$ were also recorded after UV-light irradiation with exposure to air (see the Supporting Information, Figures S14–S17). Their ^{1}H NMR spectra showed similar changes following UV-light irradiation: the signals at $\delta = 6.90$ ppm completely disappeared and new signals at around $\delta = 6.80$, 7.00, and 8.20 ppm emerged. Hence, the TPE cores of compounds $\mathbf{1_0}$, $\mathbf{1_1}$, $\mathbf{1_2}$ and $\mathbf{1_3}$ underwent transformation into 9,10-diphenylphenanthrene after UV-light irradiation for different periods.

Interestingly, the fluorescence intensity at 387 nm of compounds $\mathbf{1_0}$, $\mathbf{1_1}$, $\mathbf{1_2}$, $\mathbf{1_3}$, and $\mathbf{1_4}$ (1.0×10^{-5} mol L^{-1} in THF) reached their maxima after UV-light irradiation for 62, 44, 50, 17, and 11 min, respectively (Figure 5). Clearly, the fluorescence intensities at 387 nm of compounds $\mathbf{1_3}$ and $\mathbf{1_4}$, which contained high-generation dendrons, increased rapidly and reached their maxima after UV-light irradiation for just short periods of time. Based on these results, we concluded that the photocyclization reactivity of the TPE core within compounds $\mathbf{1_0}$, $\mathbf{1_1}$, $\mathbf{1_2}$, $\mathbf{1_3}$, and $\mathbf{1_4}$ could be modulated by the dendrons on their peripheries; the TPE core became more-photoreactive with increasing dendron-generation number, and the photoreactivity increased in the order: $\mathbf{1_0} < \mathbf{1_1} < \mathbf{1_2} < \mathbf{1_3} < \mathbf{1_4}$. This observation agreed with the ^{1}H NMR data of compounds $\mathbf{1_0}$, $\mathbf{1_1}$, $\mathbf{1_2}$, $\mathbf{1_3}$, and $\mathbf{1_4}$ (see the Supporting Information, Figures S14–S18): the signal at $\delta = 6.90$ ppm disappeared and new signals at around $\delta = 6.80$, 7.00, and 8.20 ppm emerged more-quickly for compounds $\mathbf{1_3}$ and $\mathbf{1_4}$ after UV-light irradiation compared to compounds $\mathbf{1_0}$, $\mathbf{1_1}$, and $\mathbf{1_2}$. This result was understood by considering that connecting high-generation dendrons to the TPE core significantly restricts the internal rotation and torsion, thereby rendering the excited state of TPE more-emissive and -reactive. This photocyclization reaction is currently under further investigation.

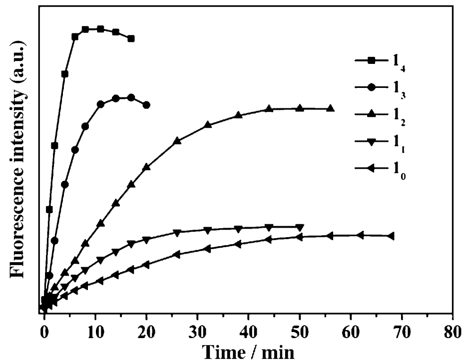


Figure 5. Plot of the fluorescence intensity at 387 nm versus the UV-light irradiation time (350 nm) for compounds $\mathbf{1_0}$, $\mathbf{1_1}$, $\mathbf{1_2}$, $\mathbf{1_3}$, and $\mathbf{1_4}$ (1.0×10^{-5} mol L^{-1} in THF).

Conclusion

Four dendron-containing tetraphenylethylene (TPE) compounds ($\mathbf{1_1}$–$\mathbf{1_4}$) were synthesized and investigated as well as a TPE compound that contained four OCH$_2$Ph groups ($\mathbf{1_0}$) for comparison. Photophysical studies were performed for compounds $\mathbf{1_1}$–$\mathbf{1_4}$, which revealed that the fluorescence of the TPE core (which was non-emissive in solution) was "switched on" after linking dendrons onto its periphery. Moreover, the fluorescence intensity was significantly enhanced when dendrons of high generation number were linked onto the TPE core; the fluorescence intensity increased in the following order: $\mathbf{1_1} < \mathbf{1_2} < \mathbf{1_3} < \mathbf{1_4}$. Based on previous studies, we presumed that this phenomenon was caused by the enhancement of the energy barrier for internal rotation and torsion of the TPE core to which four dendrons were connected. In addition, compared to compound $\mathbf{1_0}$, photocyclization of the TPE core into the respective 9,10-diphenylphenanthrene was facilitated for TPE compounds with high-generation dendrons. Again, the photocycliztion reactivity increased in the order: $\mathbf{1_1} < \mathbf{1_2} < \mathbf{1_3} < \mathbf{1_4}$. Therefore, the fluorescence and photocyclization reactivity of TPE could be modulated by covalent connection with dendrons, and such modulation was strongly dependent on the generation number of the dendrons.

Experimental Section

Physical measurements and instrumentation: Melting points were measured on a Shimadzu DTG-60. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. MS spectra were determined with BEFLEX III for TOF-MS. Elemental analysis was performed on a Flash EA 1112 Elemental Analyzer. Absorption spectra were recorded on a Hitachi (model U-3010) spectrophotometer. Fluorescence measurements were carried out on a Hitachi (model F-4500) spectrophotometer. Fluorescence decays were recorded by using an Edinburgh Analytical Instruments (FLS920) apparatus; the fluorescence lifetimes were estimated by fitting the fluorescence decays. Dynamic light scatting (DLS) was carried out on an ALV5000 Laser Light-Scattering Instrument. Preparative HPLC was performed with a recycling preparative HPLC system (JAIGEL, LC-9101).

Photocyclization: A solution of the dendron-containing TPE compound under investigation was placed into a quartz cell (path length: 1.0 cm) at RT for UV-light irradiation. Irradiation was carried out by using a PLS-SXE300UV xenon arc lamp (Beijing Trusttech Co. Ltd). Irradiation at 350 nm was achieved by using the appropriate light filters. The distance between the center of the quartz cell and the lamp was 20.0 cm; at this position, the light intensity without passing through the filters was 92 mW cm^{-2}.

Molecular-dynamic (MD) simulation: To find stable configurations of these dendron-containing TPE compounds, MD simulations under orthogonal projections to latent structures force field (OPLSFF) were performed. For compound $\mathbf{1_3}$, the total energy converged after 5 ns NPT steps. All calculations were done with GROMACS.[19]

Synthesis of compound $\mathbf{1_1}$: A mixture of tetrakis(4-hydroxyphenyl)ethylene (32 mg, 80 µmol), G_1-Br (153 mg, 0.4 mmol), KI (212 mg, 1.28 mmol), K_2CO_3 (177 mg, 1.28 mmol), and a catalytic amount of [18]crown-6 was heated to reflux in acetone (6 mL) overnight. The product was concentrated under reduced pressure and purified by column chromatography on silica gel (100–200, petroleum ether/CH_2Cl_2, 1:2). Compound $\mathbf{1_1}$ was obtained as a white powder (0.10 g, 77.9 %). M.p. >333 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.49–7.28 (m, 40 H), 6.94 (d, J = 6 Hz, 8 H), 6.70 (d, J = 7.6 Hz, 8 H), 6.65 (s, 8 H), 6.56 (s, 4 H), 5.01 (s, 16 H), 4.90 ppm (s, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 160.3, 157.2, 139.6, 138.6, 137.3, 136.9, 132.7, 128.7, 128.2, 127.7, 114.1, 106.6, 101.7, 70.3, 69.9 ppm; MS (MALDI-TOF): m/z calcd. for $C_{110}H_{93}O_{12}$: 1605.7 $[M+H]^+$; found: 1605.7; elemental analysis calcd (%) for $C_{110}H_{92}O_{12}$: C 82.27, H 5.77; found: C 81.85, H 6.21.

Synthesis of compound $\mathbf{1_2}$: A mixture of tetrakis(4-hydroxyphenyl)ethylene (16 mg, 40 µmol), G_2-Br (161 mg, 0.2 mmol), KI (106 mg, 0.64 mmol), K_2CO_3 (88.3 mg, 0.64 mmol), and a catalytic amount of [18]crown-6 was heated to reflux in acetone (6 mL) overnight. The product was concentrated under reduced pressure and further purified by column chromatography on silica gel (100–200, CH_2Cl_2/EtOAc, 40:1). Compound $\mathbf{1_2}$ was obtained as a white powder (105 mg, 79.5 %). M.p. >331 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.58–7.26 (m, 80 H), 6.92 (d, J = 5.6 Hz, 8 H), 6.77–6.58 (m, 32 H), 6.57–6.41 (m, 12 H), 4.98 (s, 32 H), 4.92 (s, 16 H), 4.86 ppm (s, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 160.3, 160.1, 157.1, 139.6, 139.4, 138.6, 137.2, 136.9, 132.8, 128.7, 128.1, 127.7, 114.1, 106.6, 106.5, 101.7, 70.2, 70.1, 69.8 ppm; MS (MALDI-TOF): m/z calcd. for $C_{222}H_{188}O_{28}Na$: 3324.3 $[M+Na]^+$; found: 3324.0; elemental analysis calcd (%) for $C_{222}H_{188}O_{28}$: C 80.71, H 5.74; found: C 80.37, H 5.89.

Synthesis of compound $\mathbf{1_3}$: A mixture of tetrakis(4-hydroxyphenyl)ethylene (8 mg, 20 µmol), G_3-Br (165 mg, 0.1 mmol), KI (53.1 mg, 0.32 mmol), K_2CO_3 (44.2 mg, 0.32 mmol), and a catalytic amount of [18]crown-6 was heated to reflux in acetone (6 mL) overnight. The product was concentrated under reduced pressure and further purified by column chromatography on silica gel (100–200 mesh, CH_2Cl_2/EtOAc, 40:1). Compound $\mathbf{1_3}$ was obtained as a white powder (113 mg, 84.3 %). M.p. >345 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.42–7.20 (m, 160 H), 6.89 (d, J = 5.6 Hz, 8 H), 6.68–6.54 (m, 64 H), 6.54–6.42 (m, 28 H), 4.92 (s, 64 H), 4.89–4.81 (m, 40 H), 4.78 ppm (s, 16 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 160.2, 160.1, 157.1, 139.6, 139.3, 138.6, 137.2, 136.9, 132.7, 128.7, 128.1, 127.7, 114.1, 106.6, 106.5, 101.7, 70.2, 70.0 ppm; MS (MALDI-TOF): m/z calcd. for $C_{446}H_{381}O_{60}$: 6695.7 $[M+H]^+$; found: 6695.0; elemental analysis calcd (%) for $C_{446}H_{380}O_{60}$: C 79.95, H 5.72; found: C 79.59, H 5.87.

Synthesis of compound $\mathbf{1_4}$: A mixture of tetrakis(4-hydroxyphenyl)ethylene (6 mg, 15 µmol), G_4-Br (251 mg, 75 µmol), KI (39.8 mg, 0.24 mmol), K_2CO_3 (33.1 mg, 0.24 mmol), and a catalytic amount of [18]crown-6 was heated to reflux in acetone (6 mL) overnight. The product was concentrated under reduced pressure and further purified by preparative HPLC ($CHCl_3$). Compound $\mathbf{1_4}$ was obtained as a white powder (0.11 g, 54.5 %). M.p. >342 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.51–7.07 (m, 320 H), 6.87 (d, J = 6.4 Hz, 8 H), 6.69–6.50 (m, 120 H), 6.50–6.25 (m, 68 H), 4.85 (s, 128 H), 4.80–4.44 ppm (m, 120 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ: 160.2, 160.1, 157.1, 139.5, 139.3, 138.6, 137.2, 136.9, 132.7, 128.6, 128.0, 127.6, 114.1, 106.5, 101.7, 70.1, 70.0 ppm; MS (MALDI-TOF): m/z calcd. for $C_{894}H_{764}O_{124}K$: 13520.3 $[M+K]^+$; found: 13520; elemental analysis calcd (%) for $C_{894}H_{764}O_{124}$: C 79.59, H 5.71; found: C 79.16, H 5.77.

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[13] This result was probably owing to the existence of different conformations of compounds $\mathbf{1_3}$ and $\mathbf{1_4}$ in solution.

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[17] Oxygen may have been dissolved in THF and it could also have been directly from the air. In addition, compound $\mathbf{2_4}$ exhibited no AIE properties as the addition of water to the solution in THF led to a fluorescence decrease (see the Supporting Information, Figure S19).

[18] ^{1}H NMR signals that were attributed to protons at positions a and b (see the Supporting Information, Figure S18) overlapped with those of the phenyl protons of the dendrons.

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