Aggregation-induced emission of dendritic phosphole oxides†

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Dendritic phosphole oxides display intense emission in the aggregate and solid states, but no emission in solution, because the intramolecular rotational motions of the peripheral dendritic groups linked to the phosphole oxide core are restricted. This unique spectroscopic feature is ascribed to an aggregation-induced emission.

Introduction

In recent years, the design and synthesis of highly emissive organic materials have been active areas of research because of their applications in optoelectronics such as organic light-emitting diodes (OLEDs).[1] A number of π-conjugated molecules have very high luminescence efficiency in dilute solutions but most of them exhibit relatively weak or no emissions when fabricated into thin films. This is because intra- and intermolecular interactions, such as π–π interactions, quench the emission process. Thus, it is difficult to obtain highly emissive materials in the solid state and also make optoelectronic devices in reality.

To overcome this obstacle, several procedures, for example, incorporation of bulky groups to the main chain for conjugated polymers, to suppress the emission-quenching processes have been proposed.[2] On the other hand, another approach, making use of the phenomenon of aggregation-induced emission (AIE) first reported by Tang and co-workers,[3,4] has attracted attention in the past few years. For example, silole, styrylbenzene, and tetraphenylethylene derivatives are found to be AIE-active.[5] AIE-active materials show no emission in solution but intense emission in aggregated or solid states and hence are promising candidates for the construction of efficient OLEDs.[6,7]

We have recently reported the synthesis and photophysical properties of phosphole- and phosphole oxide-core dendrimers,[8] which are π-conjugated organophosphorus materials that have attracted considerable interest.[9] Here we show that the dendritic phosphole oxides **1a–d** (Chart 1) are AIE-active and also discuss the key structural factors which lead to the expression of AIE.

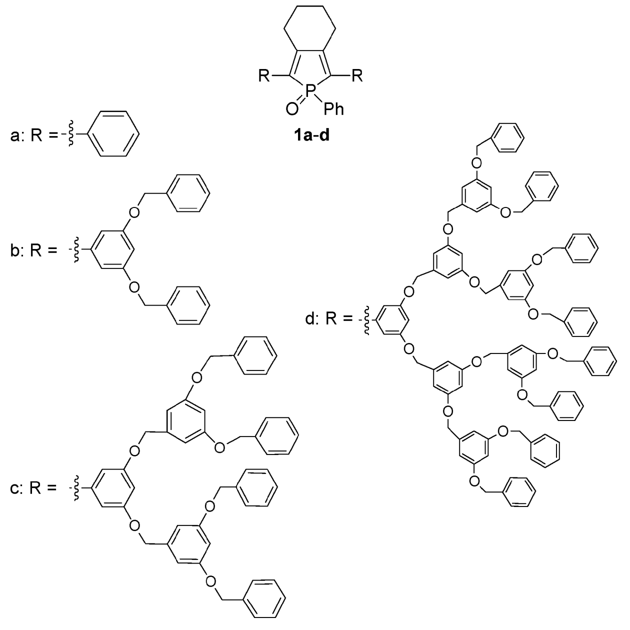

Chart 1

Results and discussion

Crystal structure analysis

To gain insight into the structure and conformation of phosphole oxides, **1a** was used as a simple model for examination by X-ray analysis. A single crystal of **1a** for X-ray analysis was obtained and analyzed to study the molecular structure and molecular packing structure. Fig. 1 shows the molecular structure of **1a**. The P=O bond length (P1–O1 = 1.489(1) Å) and P–C bond lengths (P1–C7 = 1.795(1) Å, P1–C10 = 1.814(1) Å) are comparable to that reported for phosphole oxides.[9] The oxygen atom is out of plane with the phosphole ring by 117°. It is interesting to note that the peripheral phenyl groups (C11–C12–C13–C14–C15–C16 and C17–C18–C19–C20–C21–C22) are twisted out of the plane of the phosphole oxide ring (P1–C7–C8–C9–C10), with a torsion angle of 46.5° and 10.11°, respectively. Hence, **1a** adopts a propeller-like, twisted conformation. In addition, the molecular packing shows that the phosphole oxide rings are arranged in an antiparallel manner probably due to the dipolar interaction of the P=O groups.[10]

Aggregation-induced emission

The dendritic phosphole oxides **1** are practically non-emissive, with quantum yields of less than 1% when dissolved in tetrahydrofuran (THF). However, when a large amount of water was added to the THF solution, with the original concentrations of **1** being maintained, the mixtures showed

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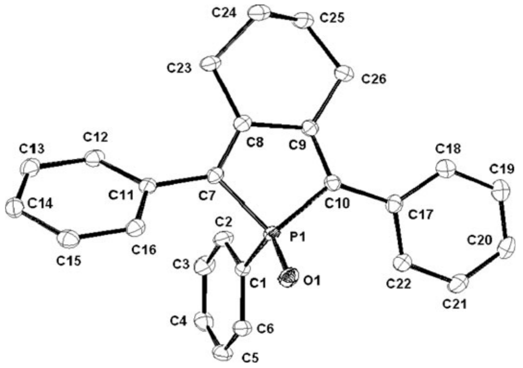

Fig. 1 ORTEP drawing of **1a**; hydrogen atoms are omitted. Ellipsoids are drawn at 50% probability. Selected bond lengths and angles: P1–C7 1.795(1) Å, P1–C10 1.814(1) Å, P1–C1 1.813(1) Å, P1–O1 1.489(1) Å, C7–C8 1.352(2) Å, C8–C9 1.501(2) Å, C9–C10 1.362(2) Å, C7–C11 1.473(2) Å, C10–C17 1.472(2) Å; C1–P1–O1 = 111.47(6)°, C7–P1–O1 = 117.46(6)°, C10–P1–O1 = 117.38(5)°, C7–P1–C1 = 106.84(5)°.

an intense emission at around 500 nm under irradiation with UV light. Fig. 2 shows photoluminescence (PL) spectra of **1b** in dilute water–THF mixtures with different water content and the resulting changes in the relative PL intensity of **1** (I/I_0, where I and I_0 are the PL intensities in a water–THF mixture and a THF solution, respectively). The PL intensity remained almost constant in water–THF mixtures with up to 50% water content but increased as the water content increased further. When the water content was increased to 90%, the PL intensity of **1b** increased to about 70 times that of the dilute THF solution of **1b**. The phosphole oxides are insoluble in water, but aggregate in water–THF mixtures with high water contents. After filtration through a 0.45 μm pore-size membrane, the filtrate still showed intense emission, indicating that the size of the aggregates is less than 0.45 μm. Dynamic light scattering (DLS) studies indicated the formation of near monodisperse particles with an average particle diameter of 117 nm in a 10% THF aqueous solution (Fig. 3). The resulting aggregation of **1b** was extremely stable; no precipitation was observed for more than a few weeks with almost no change of the PL intensity. In addition, the position and full width at half maximum of the PL for the aggregates did not change with the water content, where the spectra were almost the same as that observed for a film of **1b** (dotted line in Fig. 2a).

The observed spectral feature results from AIE. As mentioned above, the X-ray analysis of the model compound suggested that the distances between two neighboring molecules are too large to allow the π–π interactions and also the intramolecular rotations of the peripheral phenyl rings on the phosphole ring are restricted. In the aggregates and solids these prevent quenching of the luminescence process to display the intense emission. This is consistent with recent studies of AIE-active molecules.[7]

All the dendritic phosphole oxides were found to be AIE-active, but the increments of PL intensity as water content changed were dependent on the substrates (Fig. 2c). The PL spectral data of **1a–d** in water–THF (9 : 1) are summarized in Table 1. Among the dendrimers tested, **1b**

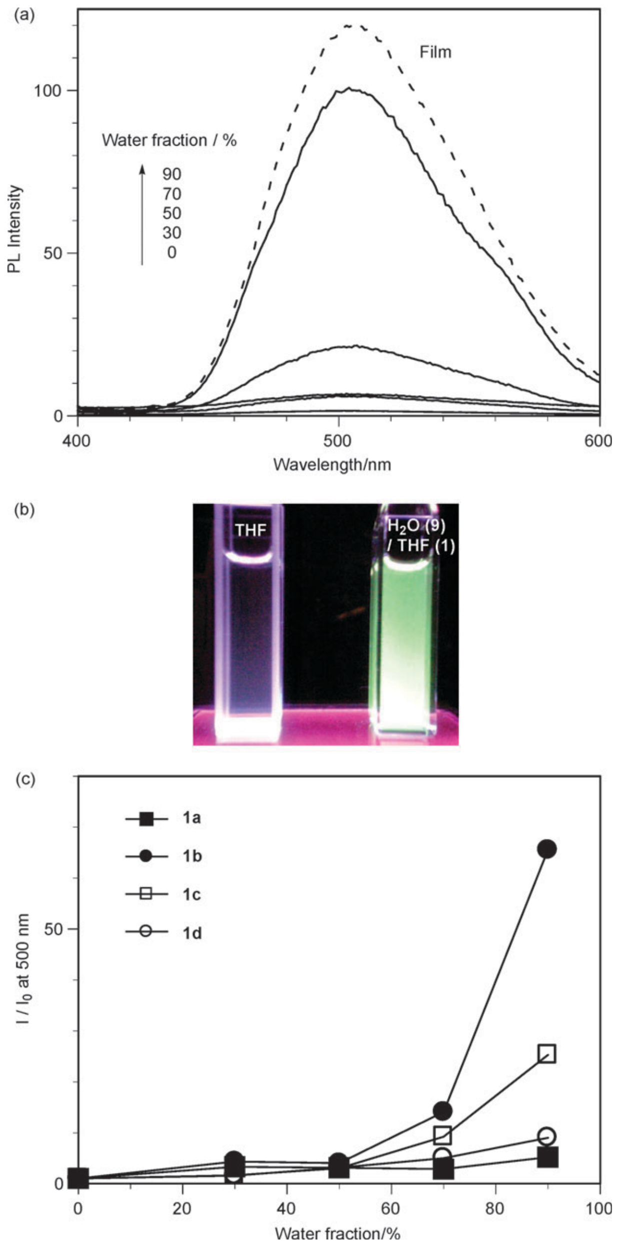

Fig. 2 (a) PL spectra (excited at 360 nm) of dilute water–THF solutions of **1b** with different water content. The dotted line shows the PL of a cast film of **1b**. (b) Photographs of **1b** in THF (left) and a mixture of H_2O and THF (v. 9 : 1) (right) under irradiation with UV light (365 nm). (c) Change in PL intensity (I) of **1a–d** with water content relative to I_0, the intensity in the THF solution, monitored at 500 nm.

showed the highest increments ($I/I_0 \approx 70$), while others gave $I/I_0 \approx 5$ (**1a**), 25 (**1c**), and 10 (**1d**) at 90% water content, probably because its combination of hydrophobic nature and polar P=O groups allows it to form stable aggregates under the set of conditions. For example, **1d** formed an aggregation with the large size at 90% water content, and the residual solution showed no emission after filtration through a 0.45 μm pore-size membrane. This is in contrast to that observed for **1b** as mentioned above. Further, the dendritic substituents affect the intramolecular rotations. **1a** has too few phenyl rings to

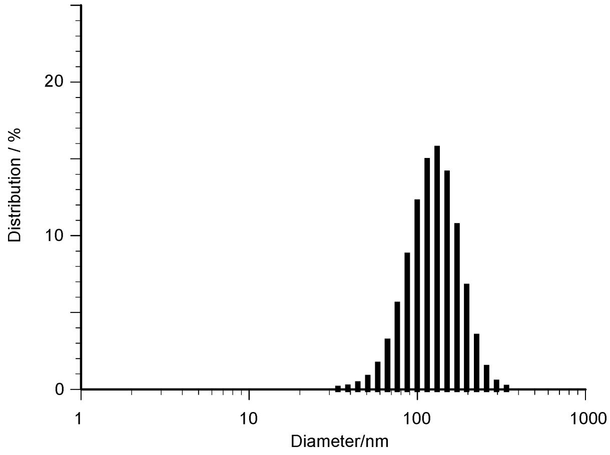

Fig. 3 DLS data of **1b** in a mixture of H_2O and THF (9 : 1 by volume). [**1b**] = 20.0 μM.

Table 1 PL spectral data of **1a–d** in water–THF (9 : 1)

Compound	$\lambda_{\text{FLmax}}{}^a$/nm	$\Phi_{\text{FL}}{}^{bc}$(%)	$I/I_0{}^d$
1a	499	0.35 [0.12]	5.2
1b	504	8.4 [0.20]	66
1c	504	12 [0.62]	25
1d	504	13 [1.6]	8

[a] Excited at the wavelength of the absorption maximum. [b] Fluorescence quantum yield determined with quinine sulfate as a standard. [c] The figures in square brackets gives the fluorescence quantum yield in THF. [d] PL intensity (I) relative to I_0, the intensity in the THF solution, monitored at 500 nm.

rotate and thus too little effect of the restricted intramolecular rotation and hence the observed minimum AIE effect. On the other hand, when too many dendrons are attached to the core, the steric crowdedness will make the intramolecular rotations difficult even in the solutions. This will make the emission difference in the solution and aggregate states small, hence reducing the AIE effect. This is probably why the AIE effect decreases on the order of **1c** to **1d**. This is also why **1b** performs the best in terms of the AIE effect. A further detailed description of the AIE characteristics of the dendritic phosphole oxides such as fluorescence lifetime measurements requires further studies.

Although the phosphole oxide aggregates displayed intense emission, the actual PL efficiencies (Φ_{FL}) should be higher than those observed in Fig. 2 and Table 1 because only the surface of the aggregates contributes to the PL spectra. On the other hand, the phosphole-core dendrimers[8] did not show a clear AIE effect because the phospholes exhibit relatively intense emissions in both dilute solutions and the solid state.

Emission under the conditions of restricted intramolecular rotation

Because the restriction of intramolecular rotations of the peripheral phenyl groups on the phosphole ring is responsible for AIE, the phosphole molecules could become more emissive in their solutions by either increasing the solution viscosity or decreasing the temperature of the sample. The effect of solvent viscosity on the emission behavior of **1b** was examined.

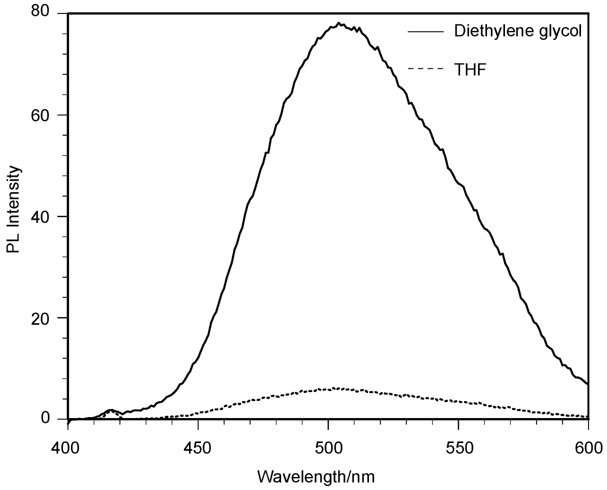

Fig. 4 PL spectra (excited at 360 nm) of **1b** in THF (dotted line) and diethylene glycol (solid line). [**1b**] = 19.0 μM.

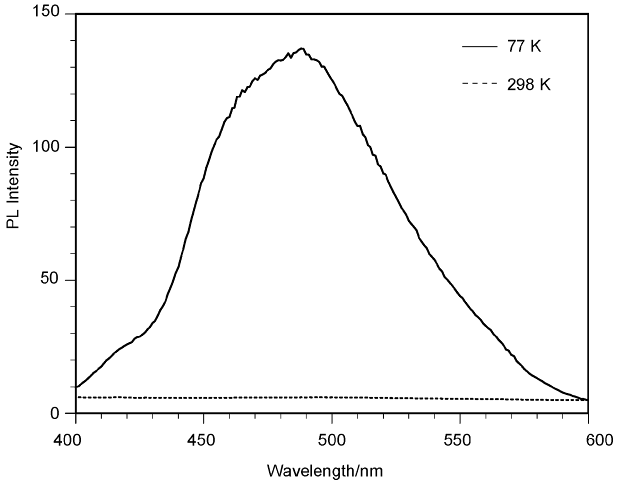

Fig. 5 PL spectra (excited at 360 nm) of **1b** in 2-methyltetrahydrofuran at 298 K (dotted line) and 77 K (solid line). [**1b**] = 19.3 μM.

Diethylene glycol was used as the solvent, whose viscosity (35.7 cp at 20 °C) is much higher than that of THF (0.55 cp at 20 °C).[11] Fig. 4 shows the PL spectra of **1b** in diethylene glycol and THF. Compound **1b** which was virtually non-emissive in THF turned emissive in diethylene glycol. The PL intensity in diethylene glycol was approximately 10-fold higher than that observed in the dilute THF solution. To study the temperature effect on the emission, the PL of **1b** in a glass matrix of 2-methyltetrahydrofuran at 77 K was also observed (Fig. 5). Under these conditions, **1b** displayed an intense emission, and its PL intensity at 77 K was ~120-fold higher than that at room temperature.

Conclusion

In this work, we have demonstrated that the dendritic phosphole oxides are AIE-active. The main cause for the AIE effect is the restriction of intramolecular rotation of the peripheral phenyl groups on the phosphole oxide ring resulting from the antiparallel dipolar arrangement and non-planar configuration of the *fluorophore* in both the aggregate and the solid states to avoid the non-radiative channel. The findings reported herein may be important for phosphole oxides and related compounds as π-conjugated systems with potential applications as optoelectronic[12] and sensory[13,14] materials. Further study is currently in progress.

Experimental

Measurements

^{1}H and ^{13}C NMR spectra were recorded using a Bruker DPX 300 FT-NMR spectrometer at 300 and 75.4 MHz, respectively. ^{31}P{^{1}H} NMR (162 MHz) spectra were recorded on a JEOL JNM-EX400 spectrometer. ^{1}H and ^{13}C chemical shifts were referenced to solvent residues. ^{31}P{^{1}H} NMR chemical shift was referenced to external aq. 85% H_3PO_4. GC-MS was run using a Shimadzu GC-MS 17A/QP-5000 mass spectrometer. High resolution mass spectra were obtained with a JEOL JMS-700 mass spectrometer at an ionization potential of 70 eV. Preparative GPC was performed on a JAI LC-908 equipped with JAIGEL 1H and 2H columns with toluene as an eluent. Melting points were measured on Micro melting point apparatus As-One IA9100. UV-Vis spectra were recorded using an Agilent 8453 photo diode array UV-Vis spectrometer. Fluorescence spectra were recorded using a Hitachi F-4500 fluorescence spectrometer. Dynamic light scattering (DLS) was obtained using a Horiba LB-550.

Materials

Phosphole oxides **1a–d** were prepared according to the previously reported procedure.[8] THF for spectroscopic measurements was distilled just before use. Water used was purified using a Millipore Milli-Q system. 2-Methyltetrahydrofuran and diethylene glycol were of reagent quality, purchased from commercial sources and used without further purification.

X-Ray crystallography

A single crystal of **1a** for X-ray analysis was obtained by addition of diethyl ether to a CH_2Cl_2 solution of **1a**. Data for **1a** were collected at −160 °C on a Rigaku Saturn CCD diffractometer equipped with monochromated Mo Kα radiation (λ = 0.71073 Å). Calculations were carried out using the program package Crystal Structure, version 3.7, for Windows. A full-matrix least-squares refinement was used for the non-hydrogen atoms with anisotropic thermal parameters. Hydrogen atoms were located by assuming the ideal geometry and were included in the structure calculations without further refinement of the parameters.

*Crystal data for **1a***: $C_{26}H_{23}OP$, M = 382.44, monoclinic a = 8.737(2), b = 14.917(4), c = 15.313(4) Å, U = 1941.5(9) Å^3, T = 113 K, space group $P21/n$ (no. 14), Z = 4, 13 782 reflections measured. The final cycle of full-matrix least-squares refinement on F was based on 3714 observed reflections ($I > 3.00\sigma(I)$). The final R factors are $R(F)$ = 0.034 and w$R(F)$ = 0.047.

Sample preparation for UV-Vis, fluorescence, and DLS measurements

A typical example is as follows. A stock solution of **1b** (1.5 mg, 1.9×10^{-3} mmol) in THF (10 mL) was prepared. To a 1 mL aliquot of the stock solution was added water (9 mL) with stirring. The mixture was then subjected to spectroscopic measurements.

Acknowledgements

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