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Photoluminescence and electroluminescence of hexaphenylsilole are enhanced by pressurization in the solid state

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Received (in Cambridge, UK) 29th February 2008, Accepted 15th April 2008
First published as an Advance Article on the web 8th May 2008
DOI: 10.1039/b803539c

Application of a hydrostatic pressure in the range of 1–650 atm boosted photoluminescence and electroluminescence of hexaphenylsilole by ~10 and ~73%, respectively, due to the suppression of intramolecular rotations and/or the increase in carrier injection, offering a helpful mechanistic insight into the intriguing phenomenon of aggregation-induced emission.

Chromophoric molecules can luminesce upon photoexcitation. The photoluminescence (PL) process is affected by a variety of internal and external factors.[1] For example, internally or structurally, a molecule with a flexible conformation often emits less efficiently than its rigid congener, because active molecular motions, such as rotation and vibration, can annihilate excited states nonradiatively. Externally or morphologically, aggregation of chromophores can quench their PL processes, due to the increase in the short-range molecular interactions and formation of such detrimental species as excimers and exciplexes.[2–9] On the other hand, aggregation can restrict molecular motions of the chromophores, which may block the nonradiative decay channels and enhance their PL efficiencies. Whether aggregation quenches or boosts a PL process depends on which of the two antagonistic effects prevails in a particular system.

Unfortunately, the negative effect of aggregation dominates the PL processes of most luminophoric molecules. The adverse effect is so often observed that it has become a "common knowledge" that aggregation quenches emission (AQE). Aluminum tris(8-hydroxyquinoline) (AlQ_3), for example, is highly emissive when dissolved in its good solvents, such as tetrahydrofuran (THF), but becomes less luminescent when aggregated in its poor solvents, such as THF–water mixtures with high water content (Fig. 1). The AQE effect thus poses an obstruction to the development of efficient organic light-emitting diodes (OLEDs), in which luminophoric materials are used as emitting layers in the solid film state.

It is of academic value and technological implication to explore new systems where aggregation plays a constructive role and to develop new ways that amplify the positive effect of aggregation.[2–9] We have previously observed that a series of silole molecules show a novel phenomenon of aggregation-induced emission (AIE).[10–13] For example, a solution of hexaphenylsilole (HPS) in acetonitrile (AN) is nonemissive but its aggregates in AN–water mixtures with high water contents are highly luminescent (Fig. 1). We have proposed that the restriction of its intramolecular rotations in the aggregates is responsible for the AIE effect.[11] An experimental proof to this mechanism is that HPS becomes emissive in solution when bulky substituents are attached to its phenyl groups to hinder its intramolecular rotations.[11b] Since pressurization can increase molecular interactions and hamper molecular motions, in this work we studied the effect of pressure on the light emission of HPS. If application of an external pressure can enhance its luminescence, it will provide an experimental support to our AIE hypothesis and an engineering means to modulate its OLED performance.

HPS was prepared according to our published procedures[11] and all other chemicals used in this study were purchased from Aldrich. HPS was deposited onto a clean quartz glass by a vapor deposition process in a vacuum chamber to form a film with a thickness of 500 nm. A thin film (150 nm) of silver was coated as a reflection layer to complete the device for PL measurement. An OLED device for electroluminescence (EL) measurement with a configuration of ITO/NPB (60 nm)/HPS (50 nm)/AlQ_3 (10 nm)/Mg : Ag (10 : 1; 200 nm)/Ag (60 nm), where NPB = *N*,*N*-bis(1-naphthyl)-*N*,*N*-diphenylbenzidine, was fabricated by depositing organic and metallic materials onto a clean and etched indium–tin oxide (ITO) $(20\ \Omega\ \square^{-1})$ glass by an evaporative deposition process. For comparison,

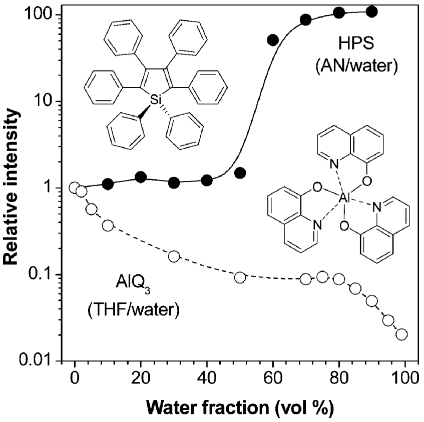

Fig. 1 Changes in PL intensities of HPS and AlQ_3 solutions with water fractions of aqueous mixtures. Solution concentration: 10 μM. Excitation wavelengths (nm): 381 (for HPS) and 489 (for AlQ_3).

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PL and EL devices of AlQ_3 were prepared by the similar procedures, with the EL device configured as follows: ITO/NPB (60 nm)/AlQ_3 (60 nm)/Mg : Ag (10 : 1; 200 nm)/Ag (60 nm).

PL spectra and EL characteristics of the devices were measured under externally applied pressures in a stainless steel high-pressure cell (HPC) with an observation window made of quartz glass. The HPC used silicon oil as pressurization medium. Pressure variations were monitored by a pressure sensor. After being sealed by a soft material, the device was fixed in the HPC with its emission side facing the observation window. Silver paste and gold wire were used to connect the electrodes of EL device to pressure-endurable electrodes of the HPC. A 404 nm laser (Power Technology Inc.) was used as the excitation light source for the PL measurement. Emission spectrum was recorded on a S2000 Miniature Fiber Optic Spectrometer (Ocean Optics). Voltage–current curve was measured on a system comprising of R6145 (Advantest) and Multimeter 2000 (Keithley).

Examples of PL spectra of the HPS film taken under different pressures are shown in Fig. 2(A). The spectral profile of the film including its curve shape and peak position is practically unaffected by the application of the external pressures, even at a pressure as high as 550 atm, indicating that the basic molecular structure of HPS is unaltered during the pressurization process. The integrated area of the PL peak, however, is sensitive to the applied pressure, exhibiting a unique effect of piezoluminescence or pressurization-enhanced emission. The PL intensity increases swiftly with increasing pressure (up to 104 atm) but starts to slowly decrease when the film is further pressurized (Fig. 2(B)). It should be noted that, at a pressure of 600 atm, the PL intensity is still higher than that of the unpressurized film.

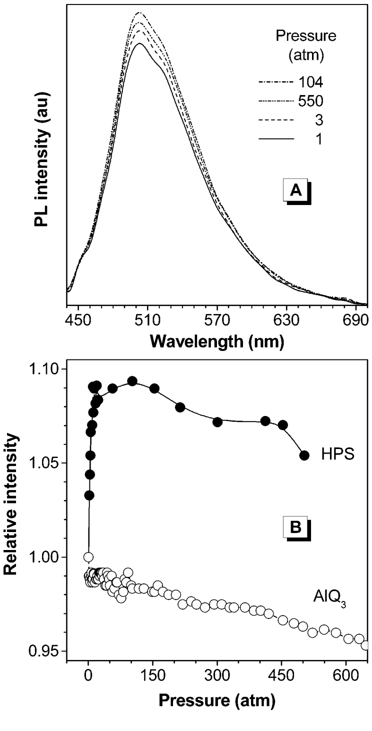

Fig. 2 (A) PL spectra of an HPS film under different pressures and (B) effects of pressure on the PL intensities of HPS and AlQ_3 films.

Compression normally weakens PL intensity of a luminophore film.[14,15] Pressurization reduces distances of adjacent molecules and increases molecular interactions, leading to enhanced possibility of electronic orbital overlapping, spin flipping, spin–orbital coupling, intersystem crossing, *etc.* These events populate the triplet state, activate energy transfer and promote excimer/exciplex formation, resulting in pressurization-induced quenching. This quenching effect is manifested by the result from the control experiment on the AlQ_3 film: its PL intensity is monotonically decreased within the pressure range of 1–650 atm (Fig. 2(B)).

Why is the PL intensity of HPS film increased by the initial pressurization? Because the bridge atom of silicon in HPS is sp^3-hybridized, the molecule of HPS is propeller-shaped with phenyl blades. When molecular interaction is strengthened, the movement of the aromatic blades becomes restricted, which shuts down the nonradiative decay channel and boosts up the PL efficiency. The molecular motions in HPS include rotation (*e.g.*, C_{Ph}–C_{silole} torsion) and vibration (*e.g.*, C_{Ph}–C_{silole} stretching and bending). The applied low pressures increase the interaction between HPS molecules but exert little effect on the distances between the groups within an HPS molecule.[16] The observed piezoluminescence effect in the low pressure region (up to 104 atm) is thus largely caused by the suppression of the molecular rotations rather than vibrations. These results are in nice agreement with our hypothesis that restriction of intramolecular rotations is the cause for the AIE effect[11] and with Shuai's theorem that low-frequency twists of the phenyl rings nonradiatively deactivate the excited states,[17,18] although further studies are needed to fully understand the AIE mechanism in detail. Restraint of intramolecular vibrational motions requires higher pressures. Further pressurization, however, activates the quenching effect, hence the observed decrease in the PL intensity of the HPS film at high pressures ($>$104 atm).

The piezoluminescence effect observed in the PL study of HPS film prompts us to explore its utility as an engineering means to modulate its OLED performance. The EL spectrum of the device (λ_{max} ~497 nm) resembles the PL spectrum of the HPS film (λ_{max} ~503 nm) but differs from that of the AlQ_3 film (λ_{max} ~536 nm), confirming that the emission is from the HPS layer. When a pressure of 22 atm is applied, the EL spectrum is instantly intensified (Fig. 3(A)). The curve shape and peak position of the EL spectrum, however, are unaltered by the application of pressure, indicating that the molecular structure of HPS and its device configuration have not been disintegrated by the pressurization. The EL intensity of the device is monotonically increased over the whole range of applied pressures (Fig. 3(B)). While pressurization of the HPS film has increased its PL intensity by up to 9%, the maximum emission enhancement effect achieved in the EL device is 73%. This $>$8-fold enhancement is due to an improvement in carrier injection, in addition to the AIE effect. The pressurization-enhanced emission is also observed in the AlQ_3 device[19,20] (Fig. 3(B)) but the effect is less pronounced, partially due to the pressurization-induced quenching effect observed in its PL process (*cf.*, Fig. 2(B)).

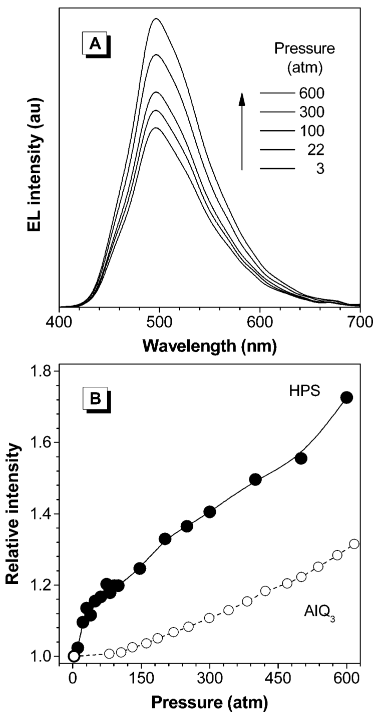

Fig. 3 (A) EL spectra of the HPS device under different pressures and (B) effects of pressure on the EL intensities of HPS and AlQ$_3$ devices at 5 V.

Current efficiencies (η_C) of the EL devices are determined by $\eta_C = aL/I$, where a = area (m^2), L = luminance (cd m^{-2}), and I = current (A).[21] As can be seen from the data plotted in Fig. 4, the current efficiency of the HPS device is increased with pressure, with a fast increase in the pressure range of 1–100 atm. The efficiency of the AlQ$_3$ device, however, is essentially independent of pressure, or even slowly decreased with pressure, in agreement with the results previously reported by Destruel *et al.*[19] The initial increase in the current efficiency of the HPS device is due to the fact that the pressurization-enhanced emission or the increase in the luminance (*cf.*, Fig. 2(B) and 3(B)) has greatly outperformed the change in the current density in the device in the low pressure region.

The positive (*e.g.*, restriction of molecular motions) and negative effects (*e.g.*, increase of molecular interactions) discussed above for the PL system are thus also at work in the EL system. However, pressurization brings some additional positive effects to an EL device, such as reduction in layer thickness, increase in interface contact, and improvement in charge injection and charge balance. As a consequence of these effects, at a given voltage, pressurization will increase current density and EL intensity. When the sum of the positive effects is larger than that of the negative ones in an OLED, its performance will be enhanced.

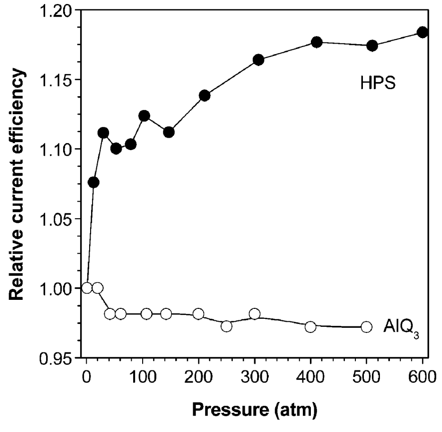

Fig. 4 Effects of pressure on current efficiencies of HPS- and AlQ$_3$-based EL devices.

In summary, in this work, we have found that the PL of the HPS film can be greatly increased by the application of a low pressure, which offers valuable mechanistic insight into the AIE process and supports our hypothesis that the restricted intramolecular rotations is the cause of the AIE effect.[5] The EL of the HPS device is also enhanced by pressurization, demonstrating that pressurization can be used as an engineering means for boosting the performance of an OLED device.

We thank Professor K.-S. Wong of the Department of Physics of HKUST for helpful discussions. This project was partially supported by the National Science Foundation of China, the Ministry of Science & Technology (973 Program) of China, and the Research Grants Council of Hong Kong under Grant Nos. 90401028, 50673003, 2002CB613405, 602706 and 603505.

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