Aggregation-induced emission of 1-methyl-1,2,3,4,5-pentaphenylsilole

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Aggregation greatly boosts emission efficiency of the silole, turning it from a weak luminophor into a strong emitter.

Many chromophoric organics and polymers are highly emissive in their dilute solutions but become weakly luminescent when fabricated into thin films.[1] This is believed to be caused by aggregate formation: in the solid state, the molecules aggregate to form less emissive species such as excimers, leading to a reduction in the luminescence efficiency. The chromophoric molecules are practically utilised in solid state commonly as thin films, and mitigation of the aggregation quenching has been a goal of research.[1,2] Many groups have attempted to obstruct aggregate formation through elaborate chemical, physical, and engineering approaches, which have, however, met with only limited success. Aggregation is in some sense inherent in film formation and it would be ideal if a molecule can emit intense light in its aggregation state. We here report such an unusual molecule, whose isolated species are faintly emissive but whose aggregates are strongly luminescent.

In our search for highly emissive linear and hyperbranched polymers,[3] we are attracted by a group of molecules called 'siloles', whose linearly drawn chemical structures appear to be conjugated, an example of which is shown in Fig. 1. During the purification process of the silole compound 1-methyl-1,2,3,4,5-pentaphenylsilole (**1**),[4] we noticed an intriguing phenomenon: when a drop of a solution of **1** was placed on a TLC plate, the wet spot could hardly be visualised with a UV lamp, but the dried spot (after solvent evaporation) was clearly visible upon UV illumination. This suggests that **1** does not luminesce when dissolved but does so upon aggregation. This rare observation prompted us to further study its luminescence behaviours.

When a dilute ethanol solution of **1** was excited at 381 nm, almost no photoluminescence (PL) signals were recorded by a spectrofluorometer (Fig. 2A). The 100-times magnified data gave a noisy spectrum; that is, **1** is indeed a weak emitter when it is molecularly dissolved in a good solvent. In contrast, when large amounts of water were added to its ethanol solutions (the final concentrations being kept unchanged at 10 µM), intense PL spectra were recorded under identical measurement conditions. Water is a non-solvent of **1** and the silole molecules must have aggregated in the solvent mixtures with high water contents. The 'solutions' were, however, macroscopically homogenous with no precipitate, suggesting that the silole aggregates are of nanodimension. A thin film of **1** prepared by

vapour deposition also gave a strong PL spectrum. The spectroscopic analyses thus confirmed our visual observation described above.

To have a quantitative picture, we estimated the PL quantum yields (Φ_F) of **1** in ethanol and water–ethanol mixtures, using 9,10-diphenylanthracene as the reference. The Φ_F value for the ethanol solution was 0.63×10^{-3} (Fig. 2B), falling in the range of the literature values (0.31–5.13×10^{-3}) of their close cousins.[5] The Φ_F value remained almost unchanged when up to 50% water was added to the ethanol solution but started to swiftly increase afterwards. When the water fraction was increased to 90%, Φ_F rose to 0.21, which is 333 times higher than that of the ethanol solution. The trajectory of the Φ_F change suggests that the molecularly dissolved **1** starts to congregate at a water fraction of 50% and the population of the aggregate continues to increase as the water fraction increases. Similar results were obtained when water was added into THF solutions of **1**. The change of the PL spectrum with solvent composition may be regarded as a special type of solvatochromism, and the sensitive on/off switching of the light emission by aggregation/deaggregation may find potential applications in optoelectronics systems.

To gain an insight into the cause of the unique PL behaviours of **1**, we checked its UV absorption spectra. The spectra of **1** in ethanol and 50% water–ethanol mixture were almost identical (Fig. 3). Its absorption bands in the 60% water–ethanol mixture, however, rose in intensity and moved to longer wavelengths. A level-off tail is seen in the visible spectral region; such tails are commonly observed in nanoparticle suspensions,[6] confirming the existence of nanoaggregates of **1** in the solvent mixture. The spectrum was further intensified as the water fraction increased. The differential spectra shown in the inset clearly manifest the growth of the red-shifted bands with an increase in the water fraction. The new peaks at ~291 and 400 nm are obviously due to the nanoaggregate absorption. When the silole molecules cluster together, its effective concentration decreases and the absorbance should also decrease. The increase in the absorbance thus indicates that the nanoaggregates are better conjugated than their counterparts of isolated species.
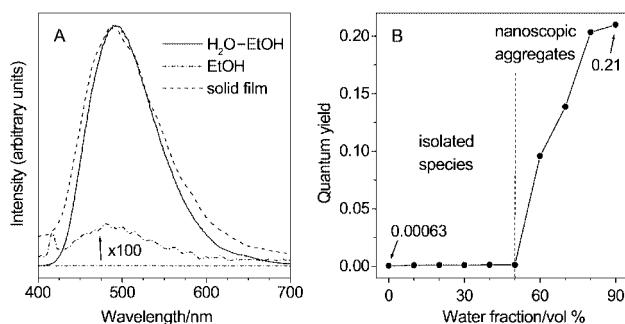

Fig. 1 Molecular structure and conformational rotamers of **1**.

Fig. 2 (A) PL spectra of **1** in water–ethanol mixture (90:10 by volume), absolute ethanol, and solid film; concentration of **1**: 10 µM; excitation wavelength (nm): 381 (for solutions), 325 (for film). (B) Quantum yield of **1** vs. solvent composition of the water–ethanol mixture.
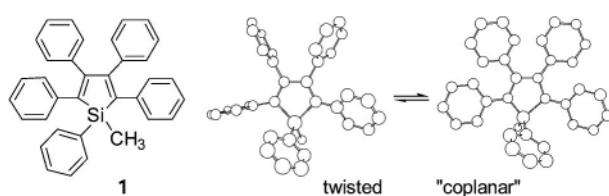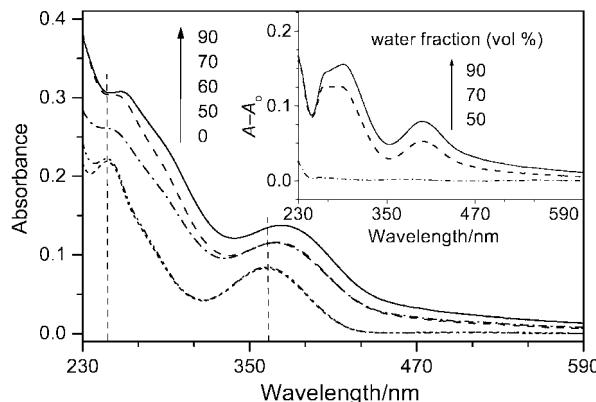
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Fig. 3 UV spectra of **1** in water–ethanol mixtures (concentration of **1**: 10 μM). Inset: differential spectra of **1** (A and A_0 being absorbance of **1** in mixture solvent and absolute ethanol, respectively).

Fig. 4 (A) PL spectra of **1**–PMMA composites (excited at 325 nm). (B) Luminance of the composite film *vs.* its content of **1**.

The silole may exist mainly as a twisted conformer when it is molecularly dissolved in a good solvent. A twisted rotamer of **1**, whose energy was minimised by the MM2 method in a CS Chem3D Pro program, is given in Fig. 1. The phenyl peripheries linked to the silole core are obviously out of coplanarity. It has been proposed that coplanarisation of chromophores can be induced by aggregation.[7] When **1** aggregates, coplanarisation of its peripheries and core may be induced to a certain extent. It is well known that coplanar and twisted conformers have different resonance energy: when the rings are on the same plane, the degree of conjugation is at a maximum; when the rings rotate to 90° to one another, the conjugation drops to a minimum. The best-known example of this is biphenyl (**2**) and its non-coplanar 2,2'-dimethyl homologue (**3**), which exhibit quite different electronic properties (*e.g.* $\varepsilon_2/\varepsilon_3 > 20$). The coplanarisation of **1** induced by the aggregation leads to a better conjugation between its peripheries and core, thus intensifying and red-shifting its absorption and emission bands. The silole molecules in the nanoaggregates cannot, however, assume a perfect coplanar conformation due to the involved steric crowdedness, and the phenyl rings may still rotate to some degree to cope with the steric repulsion. Such rotation will preclude co-facial alignment of the molecules and hinder excimer formation.[7] Aggregation quenching thus cannot operate in the luminescence process of **1**.

To further verify that aggregation quenching is not involved and to prove the usefulness of the novel luminescence property, we carried out a solid-state 'dilution' experiment and prepared a series of composite films of **1** and poly(methyl methacrylate) (PMMA). The compatibility of **1** and PMMA enabled us to cast thin films of optical quality from its chloroform solutions. The progressive red-shift of the PL spectrum with an increase in the content of **1** manifests the formation and population of the nanoaggregates in the solid 'solutions' (Fig. 4A). The linear increase of the luminance with the content of **1** testifies that the light emission is not quenched by aggregation. The composite film with 90% of **1** emitted a blue light of 492 nm with a high luminance of ~ 24000 cd m^{-2}. We built an electroluminescence (EL) device of ITO/CuPc/TPD/**1**/Mg-Ag,† which emitted a blue light of 496 nm. When an Alq$_3$† layer was introduced, the device ITO/CuPc (20 nm)/TPD (50 nm)/**1** (50 nm)/Alq$_3$ (10 nm)/LiF-Al showed a low turn-on voltage (3.4 V), high emission efficiencies (9234 cd m^{-2}, 12.6 lm W^{-1}, and 12 cd A^{-1}) and external quantum yield (8%). When the thickness of the Alq$_3$ layer was optimised (7 nm), the power efficiency was boosted to 20 lm W^{-1}. The silole is thus an excellent light-emitting material for the device application.
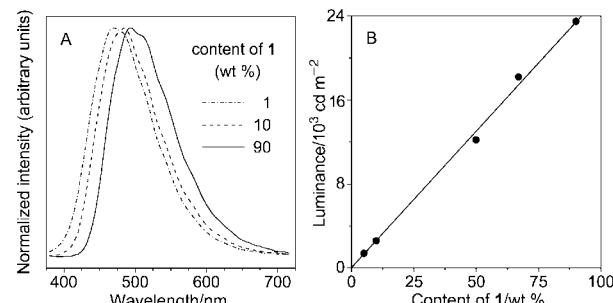
In summary we revealed the uncommon emission behaviours of a silole (**1**) in this study. It has been a common 'law' that aggregation quenches light emission. What we observed here is exactly the opposite: light emission is induced by aggregation. The aggregation increased the emission efficiency of **1** by as high as two orders of magnitude (333 times). This is exceptionally rare, if not unprecedented, for small organic molecules.[8] Aggregation quenching has been the thorniest problem in the development of organic light-emitting diodes with high efficiencies. Our finding of aggregation-induced emission may stimulate new molecular engineering endeavours in the design of luminescent organics and polymers with highly emissive aggregation states.

Notes and references

† ITO = indium–tin oxide, CuPc = copper phthalocyanine, TPD = *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-diphenyl-4,4'-diamine, Alq$_3$ = tris(8-hydroxyquinolinato)aluminum.

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