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Tetrabenzo[5.7]Fulvalene: A Forgotten Aggregation Induced-Emission Luminogen

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Tetrabenzo[5.7]fulvalene, one of the first recognized stable members of mixed fulvalenes, has attracted widespread interest for its remarkable structure. However, little has been known about its photoactivity, most likely owning to its very weak luminescence in solution state. Here we show for the first time that this compound exhibits aggregation-induced emission (AIE) properties. Its photoluminescence and X-ray crystal structure reveal an interesting mechanism of AIE phenomenon.

The fulvalene family is a unique class of organic compounds that consist of two cross-conjugated rings through a double bond.[1] Tetrabenzo[5.7]fulvalene (Figure 1) was recognized as one of the first stable members of mixed fulvalenes.[1] It has attracted widespread interest for its unusual structural framework. Tetrabenzo[5.7]fulvalene has been employed as a model system for studies of the nature of aromatic bonding,[2] as partial aromatic nature can be introduced to one or both rings via electronic modifications.[3] However, little has been known about its photoactivity, most likely owning to its almost negligible luminescence in solution state.

Structurally, the compound possesses a peculiar framework combining the [5.7]fulvalene (highlighted in red, Figure 1) with the tetraphenylethylene (TPE, highlighted in blue) skeletons. TPE is the primary and most frequently used building block for aggregation-induced emission (AIE) materials.[4] AIE is a term coined by Tang and co-workers in 2001[5] where molecules display limited photoluminescence in solution but show enhanced emission in aggregated form.[4] Based on our previous works on AIE luminogens[6] as well as the chemistry of the seven-membered ring tropylium ion[7] and its related organic dyes,[8] we are interested in investigating further into the AIE behaviour of this particular compound. Indeed, this work shows that tetrabenzo[5.7]fulvalene exhibits strong AIE properties, which, interestingly, has never been reported.

Some related systems to tetrabenzo[5.7]fulvalene have been studied for aggregation-induced emission. In 2014, Tang and co-workers has reported that [7,7] fulvalene 10,10′,11,11′-tetrahydro-5,5′-bidibenzo[a,d][7]-annulenylidene (**THBDBA**, Figure 1) was shown to exhibit AIE activity due to restriction of intramolecular vibrations.[9] The tethered phenyl rings of THBDBA are predicted to exist in both the lower energy 'boat' and the higher energy 'chair' conformations and free interchangeability between the two conformers could lead to non-radiative decay of excited-state energy. This conformational change is inhibited in aggregated form, leading to AIE phenomenon. The fully conjugated analogue (**BDBA**, Figure 1) also showed AIE activity to a lesser extent.[9] More recently in 2018, Campaña and co-workers reported a family of cumulene derivatives (Figure 1) and showed that they also displayed AIE behaviour[10] due to steric restriction of their intramolecular rotations in aggregated form.

In order to study the AIE characteristics of tetrabenzo[5,7]fulvalene (**1**, Scheme 1), the compound was prepared according to a modified literature procedure[11] in two simple steps (see page S5 in the ESI).[12] Solutions of **1** in DCM,

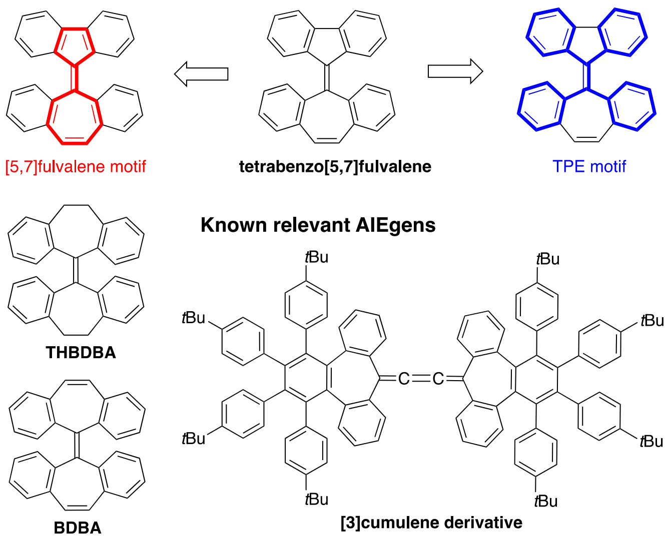
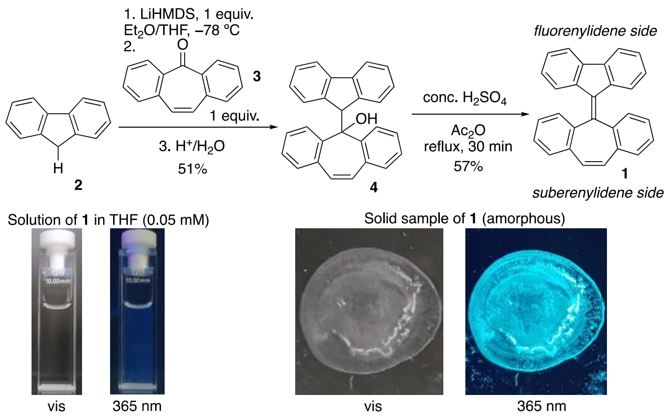


Figure 1. Tetrabenzo[5,7]fulvalene and related AIE luminogens (AIEgens)



Scheme 1. Synthesis of tetrabenzo[5,7]fulvalene **1**

MeCN and THF were not visibly luminescent. To our delight, however, upon being irradiated with 365 nm UV light the solid sample emitted an intense light blue colour (Scheme 1), suggesting that this compound might exhibit AIE activity.

UV-vis absorption and fluorescence spectra of a solution of tetrabenzo[5.7]fulvalene **1** in THF at 0.05 mM concentration were subsequently measured. It absorbs in the UV range, with an absorbance peak at 317 nm (Figure 2, top-left). Excitation at

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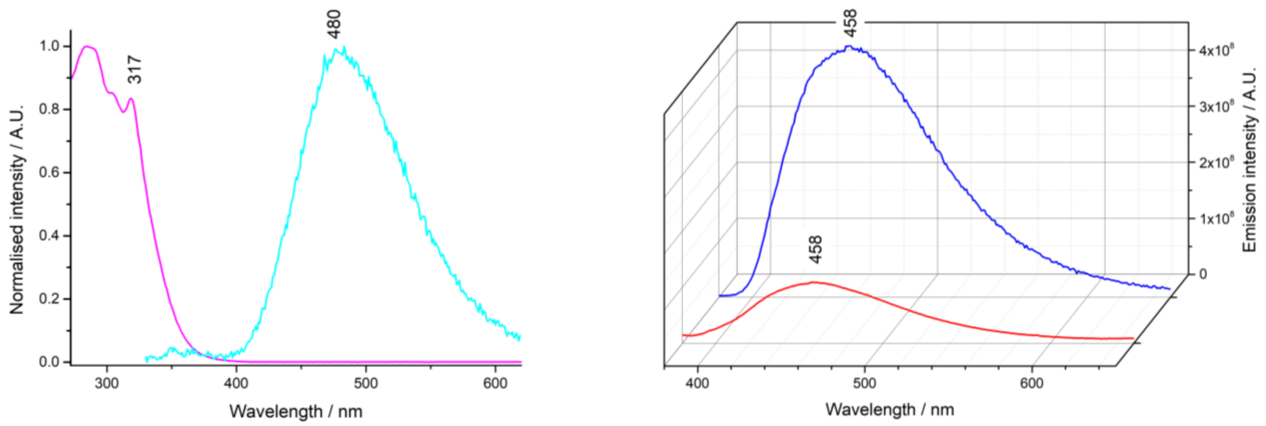
317 nm led to a weak emission maximum at 480 nm (Figure 2, top-left), with a Stokes shift of 163 nm (10,712 cm^{-1}). This emission peak is red-shifted comparing to that of TPE (377 nm when excited at 280 nm in the same solvent).[9] The absorption spectrum of **1** as thin film resembled that of solution spectrum, with an absorption maximum of 328 nm (see pageS11 in the ESI).[12] Unfortunately, it is technically difficult to obtain a UV-vis absorption spectrum of the crystalline solid form because of scattering. The emission spectra of **1** in both thin film and crystalline solid revealed identical emission maximum of 458 nm (Figure 2, top-right), slightly blue shifted from the emission peak in solution state. Interestingly, the emission intensity of the compound in crystalline form was much higher than those of both thin film and solution.

An initial assessment of the AIE behaviour in solution form was undertaken by varying the amount of water, an anti-solvent, added to a stock solution of **1** in THF while keeping its total concentration the same (0.05 mM). With water fraction (f_w) varying between 0 and 70%, no significant change in fluorescence occurred (Figure 3). From $f_w \geq 75\%$, a significant increase in fluorescence was observed up to f_w of 95% (Figure 3). This standard study unquestionably confirmed the AIE behaviour of compound **1**.

Quantum yield measurements revealed only feint fluorescence of tetrabenzo[5.7]fulvalene in THF solution, with $\Phi_{soln} < 0.1\%$ as the emission is too weak to obtain a reliable value in the integrating sphere or by comparative method.[12] Interestingly, thin film quantum yield was measured to be much higher, Φ_{tf} = 20.2%, over 200-time increase, and crystalline solid was measured at a remarkable Φ_{cryst} = 34.7%, an almost 350-time increase from the fluorescence efficiency of compound **1** in solution (Figure 2 table).[12] Most remarkably, the Φ_{AIE} of the aggregate sample in 90% water and 10% THF was 43.2±0.2%, over 430-time increase from that of the THF solution. This clearly demonstrates that tetrabenzo[5.7]fulvalene can potentially served as a better AIE building block than BDBA, THBDBA or even TPE (Figure 1), as the similar aggregation-induced emission factors (α_{AIE}) for these compounds are 60, 230 and 344, respectively (Figure 3, bottom).[9]



	PLQY (%)	PL lifetime
Solution THF	< 0.1 [*]	2.3 ns
Solution water/THF=9:1	43.2 ± 0.2	33.3 ns
Thin-film	20.2 ± 0.3	31.6 ns
Crystalline	34.7 ± 0.1	35.4 ns

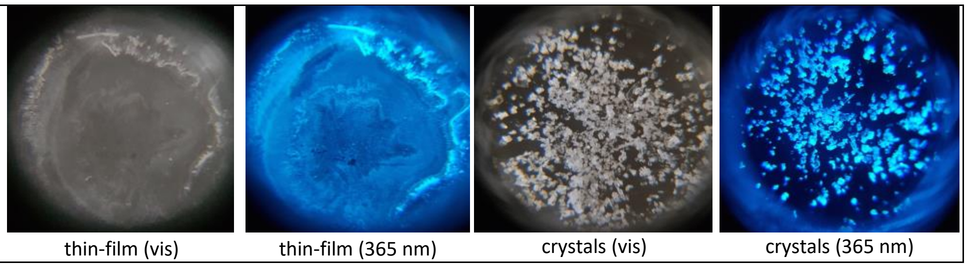


Figure 2. (**top-left**) Normalized UV-vis absorption(purple) and fluorescence spectra (cyan, excited at 317 nm) of **1** in solution (THF, 0.05 mM); (**top-right**) fluorescence spectra (excited at the laser setting of the spectrometer = 365 nm) of **1** in thin-film (red) and crystalline (blue) forms; (**bottom-left**) Photoluminescent quantum yields and lifetimes; (**bottom-right**) Photos of **1** in thin-film and crystalline forms. [*]The emission in THF solution is too weak to obtain a reliable value in the integrating sphere.

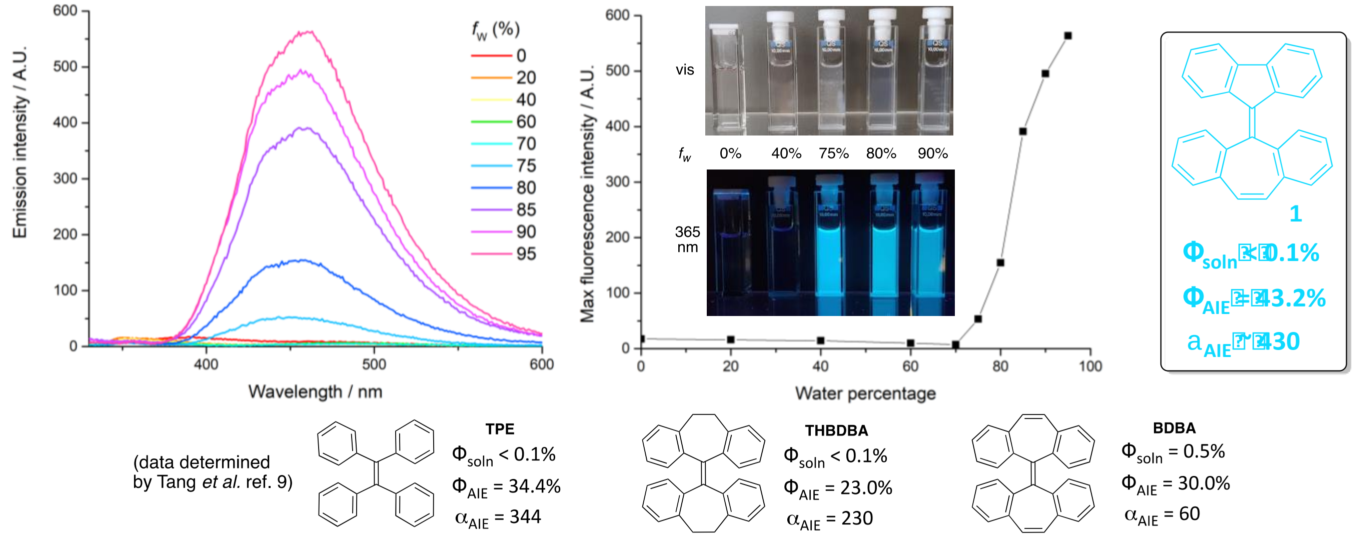


Figure 3. (**top-left**) Emission spectra of tetrabenzo[5.7]fulvalene **1** in THF with varying f_w (total concentration of **1** = 0.05 mM), λ_{ex} = 317 nm; (**middle**) Plot of maximum emission intensity of **1** in THF with varying f_w (total concentration of **1** = 0.05 mM), λ_{ex} = 317 nm; (**inset**) Photos of solutions of **1** in THF with varying f_w (total concentration of **1** = 0.05 mM).

The enhancement of AIE phenomenon of **1** in comparison to TPE (Figure 3) is very intriguing as rigidified TPE derivatives such as the aforementioned BDBA and THBDBA are both less AIE-genic than TPE itself (Figure 3, bottom).[9] Similar diminishing effect by tethering was also previously observed with tetrathienylethene (TTE), another TPE analogue reported by Tang and co-workers.[13] In the case of **1**, we believe that the contribution of the fulvalene-type motif (Figure 1) probably plays a crucial role behind its unusual AIE.

The fluorescence lifetime of the samples were also measured (Figure 2 table, also see page S13 in the ESI).[12] The lifetime of the solution sample was shorter than the thin film and crystalline samples, presumably due to the fast non-radiative decay processes in solution.[14] The aggregated sample in 90% water in THF has fluorescence lifetime comparable to those of the thin film and crystalline samples. It is noteworthy that the fluorescent lifetime of tetrabenzo[5,7]fulvalene **1** in aggregates were longer than most TPE derivatives known to date.[4,15] This can be attributed to the greater rigidity of **1** that further reduces the non-radiative pathways.

To understand the mechanism of AIE phenomenon of **1**, X-ray crystal structure[16] of this compound was obtained. Tetrabenzo[5.7]fulvalene **1** exhibited a high level of symmetry in the crystal structure (Figure 3a), due to negligible deviation of benzo groups on both suberenylidene and fluorenylidene sides. The C-C bond joining the two tricyclic groups was measured at 1.349 Å (Figure 3a), indicative of a double bond, which would certainly assist in rigidifying the compound. Also apparent in the crystal structure is an intramolecular C-H – π interaction from the C-Hs on the fluorenylidene moiety to the benzene rings of the suberenylidene group, with a distance of *ca.* 2.778 Å (Figure 3a). These weak interactions might assist in further rigidifying the molecule.

The ethylene tether of the suberenylidene moiety does not serve as a conjugation bridge between two benzo groups. The dihedral angle on the suberenylidene moiety was extremely large at 120.15° (Figure 3b). This is most likely due to the steric clash between benzo groups from both suberenylidene and fluorenylidene motifs. The suberenylidene was bent into a saddle shape, which is a very important feature for the AIE behaviour of the compound, as it inhibits intermolecular π–π stacking interaction not only between suberenylidene but also fluorenylidene units (*vide infra*, Figure 3d).

Interestingly, there are double C-H – π interactions between the C-Hs of the ethylene tether on one molecule to the benzo groups of the suberenylidene moiety on another molecule, with a distance of ~2.675 Å (Figures 3c). Even more remarkable is the behaviour of adjacent fluorenylidene moieties (Figure 3d). One side of the fluorenylidene has intermolecular C-H – π interactions within a short distance of 2.744 Å with another fluorenylidene unit. The opposite side of the same motif is completely blocked by several highly distorted suberenylidene moieties (distance = 2.889 Å in Figure 3d). This results in some interlocking effects that reduce molecular motions (rotational or vibrational), leading to the high quantum yield of the crystalline form (Φ_{cryst} = 34.7%) and the aggregates (Φ_{AIE} = 43.2%). Finally, although the distance between the planes containing fluorenylidenes is very small (1.128 Å in Figure 3e), there are no intermolecular π–π interaction between these fluorenylidene moieties as they do not overlap (Figure 3d).

The mechanism of AIE behaviour for TPE is explained by rotations of pendant phenyl groups in solution state, which are restricted in aggregate form.[4] The benzene rings in the suberenylidene moiety in tetrabenzo[5.7]fulvalene **1** are tethered and not as flexible as pendant phenyl groups. Furthermore, the fluorenylidene motif in compound **1** is almost planar, only allowing for marginal intramolecular movements. Therefore, the most likely intramolecular movements causing non-radiative decay in tetrabenzo[5.7]fulvalene would be the 'flapping' of the two benzo wings on the suberenylidene moiety. Restriction of these movements in aggregates by a combination of inter- and intra-molecular C-H – π interactions, as discussed above, presumably leads to the AIE phenomenon for compound **1**.

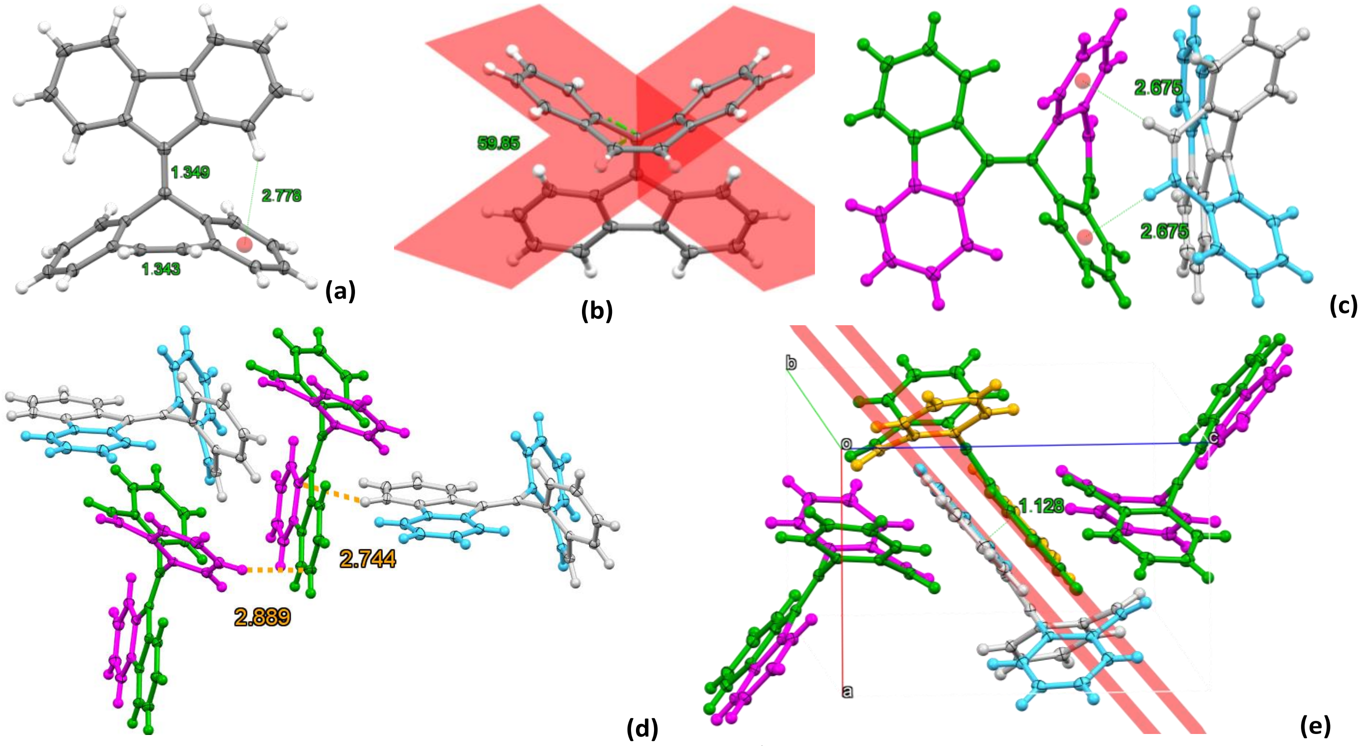


Figure 3. X-ray crystal structure of tetrabenzo[5.7]fulvalene **1**. All bond lengths and distances are in Å.

In conclusion, tetrabenzo[5.7]fulvalene, a so far forgotten luminogen, was shown to be AIE-active with good quantum yields in thin film (Φ_{tf} = 20.2%), crystalline solid (Φ_{cryst} = 34.7%) and solution aggregates (Φ_{AIE} = 43.2%). The causes of AIE phenomenon for this compound differs from that of the parent TPE motif. Further studies on this framework should give more insights into the yet not fully understood mechanism of AIE and pave the way for its potential opto-electronic applications.

Conflicts of interest

There are no conflicts to declare.

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