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

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Reece D. Crocker,^a Bolong Zhang,^b Domenic P. Pace,^a Wallace W. H. Wong,^b Thanh V. Nguyen,^{*a}

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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 owing 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 owing 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 2001⁵ where molecules display limited photoluminescence in solution but show enhanced emission in aggregated form.⁴ Based on our previous works on AIE luminogens⁶ as well as the chemistry of the seven-membered ring tropylium ion⁷ 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 aggregation-induced emission properties, which, interestingly,

has never been reported in literature.

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]-annulenyldiene (**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 The saddle-shaped polyphenyl-substituted endgroups were thought to turn on the emission of the [3]cumulene by steric protection and restriction of their intramolecular rotations in aggregated form.

Figure 1. Tetrabenzo[5.7]fulvalene and related AIE luminogens (AIEgens)

^a School of Chemistry, University of New South Wales, Sydney, Australia
E-mail: t.v.nguyen@unsw.edu.au

^b ARC Centre of Excellence in Exciton Science, Bio21 Institute and School of Chemistry, University of Melbourne, Australia

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

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 Alcohol **4** could be readily synthesized by nucleophilic addition of *in situ* generated fluorenone from fluorene (**2**) to dibenzosuberone (**3**). Subsequent dehydration of tertiary alcohol **4** with concentrated sulfuric acid in acetic anhydride afforded the target compound in good overall yield after

column chromatography and recrystallization.¹² Preliminary tests showed that solutions of **1** in DCM, MeCN and THF were not visibly photoluminescent. 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 as predicted.

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 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 page S11 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 (see page S3 in the ESI for sample preparation), suggesting that the compound is more luminescent in crystalline form.

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. Solution = soln; Thin-film = tf; Crystalline = cryst.

Figure 3. (left) Emission spectra of tetrabenzo[5,7]fulvalene **1** in THF with varying water percentages (total concentration of **1** = 0.05 mM), $\lambda_{\text{ex}} = 317$ nm; (right) Plot of maximum emission intensity of tetrabenzo[5,7]fulvalene **1** in THF with varying water percentages (total concentration of **1** = 0.05 mM), $\lambda_{\text{ex}} = 317$ nm; (inset) Photos of solutions of **1** in THF with varying water percentages (total concentration of **1** = 0.05 mM).

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 $\Phi_{\text{soln}} < 0.1\%$ 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, $\Phi_{\text{tf}} = 20.2\%$, over 200-time increase, and crystalline solid was measured at a remarkable $\Phi_{\text{cryst}} = 34.7\%$, an almost 350-time increase from the fluorescence efficiency of compound **1** in solution.¹² Most remarkably, the Φ_{AIE} of the aggregate sample in 90% water and 10% THF was $43.2 \pm 0.2\%$, 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 BDDBA, THBDDBA or even TPE (Figure 1), as the similar aggregation-induced emission factors (α_{AIE}) for these compounds are 60, 230 and 344, respectively (Figure 4).⁹

The enhancement of AIE phenomenon in tetrabenzo[5,7]fulvalene **1** in comparison to TPE (Figure 4) is very intriguing as rigidified TPE derivatives such as the aforementioned BDDBA and THBDDBA are both less AIE-genic than TPE itself (Figure 4). Similar diminishing effect by tethering was also observed with tetrathienylethene (TTE), another TPE analogue reported by Tang and co-workers.¹³ When the aromatic rings of TTE are bridged as in si-TTE and fi-TTE, they become less AIE then TTE (Figure 4).¹³ In the case of tetrabenzo[5,7]fulvalene **1**, we believe that the intramolecular bridges can force the molecule into a fulvalene-type motif (as highlighted in Figure 1), which is something to take into

consideration for any possible explanation of its unusually high AIE factor and quantum yield.

The fluorescence lifetime of the samples were also measured (Figure 2 table, also see page S13 in the ESI).¹² As previously observed for typical AIE compounds, the lifetime of the solution sample was shorter than the thin film and crystalline samples due to the fast non-radiative decay processes in solution.¹⁴ The aggregated sample in 90% water in THF has fluorescence lifetime of 33.3 ns, which is 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 tetrabenzo[5,7]fulvalene **1** that further reduces the non-radiative pathways.

To further understand the mechanism of AIE phenomenon of tetrabenzo[5,7]fulvalene **1**, X-ray crystal structure¹⁶ of this compound was obtained with a sample recrystallized from hot

Figure 4. Tetrabenzo[5,7]fulvalene and related AIE luminogens (AIEgens)

Figure 4. X-ray crystal structure of tetrabenzo[5.7]fulvalene **1**. All bond lengths and distances are in Å.

toluene solution. Tetrabenzo[5.7]fulvalene **1** exhibited a high level of symmetry in the crystal structure (Figure 4a), 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(2) Å (Figure 4a), indicative of a double bond, which would certainly assist in rigidifying the compound. It suggests that the intramolecular charge-transfer, typically observed with [5.7]fulvalene, might not be favourable for the tetrabenzosubstituted system in **1**.

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 calculated distance of 2.778 Å (Figure 4a). These weak interactions might assist in further rigidifying the molecule,

which could explain the high quantum yield and PL lifetimes in thin film, a less ordered solid. The ethylene tether of the suberenylidene moiety, while rigidifying the structure, 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 4b). 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, 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 4e).

Interestingly, there are double intermolecular 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 calculated distance of 2.675 Å (Figures 4c and 4d, two views from different angles). Even more remarkable is the behaviour of adjacent fluorenylidene moieties (Figure 4e). As can be seen from the crystal packing, 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 4e). This may result 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 4f), there are absolutely no intermolecular π – π stacking interaction between these fluorenylidene moieties as they do not overlap (Figure 4e).

Despite the similarities between tetrabenzo[5.7]fulvalene **1** and tetraphenylethylene (TPE, Figure 1), crystal structure analysis suggests that the two molecules behave differently to each other in their AIE. 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 Due to the rotation inhibition of the unsaturated tether, the benzene rings in the suberenylidene moiety of **1** are not as flexible as pendant phenyl groups. Furthermore, the fluorenylidene motif in compound **1** is almost completely 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**.

In conclusion, tetrabenzo[5.7]fulvalene 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, so further studies on this framework should give more insights into the yet not fully understood mechanism of AIE. Furthermore, given that the structure of tetrabenzo[5.7]fulvalene is highly tuneable via a simple synthetic protocol (Scheme 1) and the compound has previously shown to exhibit redox behaviour,¹ this work paves the way for potential opto-electronic applications of tetrabenzo[5.7]fulvalene, a so far forgotten AIE luminogen, and its derivatives.

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Conflicts of interest

There are no conflicts to declare.

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16. Atomic coordinates, bond lengths and angles and displacement parameters for tetrabenzo[5.7]fulvalene has been deposited at the Cambridge Crystallographic Data Centre (CCDC No. 1910665). This data can be obtained free-of-charge via http://www.ccdc.cam.ac.uk/data_request/cif.