Synthesis of superstructures of AIE active tetraphenylethylene through solvophobic controlled self-assembly

A thesis submitted in fulfilment of the requirements for the degree of Master of Science

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October 2017
Declaration

I certify that, except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program; any editorial work, paid or unpaid, carried out by a third party is acknowledged; and, ethics procedures and guidelines have been followed. I acknowledge the support I have received for my research through the provision of an Australian Government Research Training Program Scholarship.

Mina Salimimarand

20/10/2017
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Publications


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## Abbreviations

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<tr>
<td>% vol</td>
<td>Volume percentage</td>
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<tr>
<td>ACQ</td>
<td>Aggregation Caused Quenching</td>
</tr>
<tr>
<td>AIE</td>
<td>Aggregation Induced Emission</td>
</tr>
<tr>
<td>BTPE-FN</td>
<td>2,3-bis(4’-(1,2,2-triphenylethenyl) biphenyl-4-yl) fumaronitrile</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper</td>
</tr>
<tr>
<td>FL</td>
<td>Fluorescence</td>
</tr>
<tr>
<td>H-bond</td>
<td>Hydrogen bond</td>
</tr>
<tr>
<td>Hg</td>
<td>Mercury</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic Light Emitting Diode</td>
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<tr>
<td>PL</td>
<td>photoluminescence</td>
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<tr>
<td>RIM</td>
<td>Restriction of Intramolecular Motion</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TEA</td>
<td>Triethylamine</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TiCl₄</td>
<td>Titanium tetrachloride</td>
</tr>
<tr>
<td>TLC</td>
<td>Thin Layer Chromatography</td>
</tr>
<tr>
<td>TPE</td>
<td>Tetraphenylethylene</td>
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<tr>
<td>UV-Vis Spectroscopy</td>
<td>Ultra violet-visible Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>Zn</td>
<td>Zinc Powder</td>
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<tr>
<td>μm</td>
<td>Micrometer</td>
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Abstract

Aggregation induced emission (AIE) is a novel type of behaviour of macromolecules that emit light under UV excitation when aggregated in the solid state. This is opposed to traditional Aggregation Caused Quenching (ACQ)–type macromolecules that quench their luminescence upon aggregation. Tetraphenylethylene is the most famous molecule that shows AIE behaviour, as it can acts as a building block in structures that can neutralize the notorious ACQ effect which is undesirable in many applications.

In this thesis, several derivatives of TPE with mono- & di-acids containing odd and even numbers of CH₂ units in the appended chains, are synthesized study the effect of odd & even carbon chains on self-assembly, and also to investigate the mechanochromic features of the resulting molecules.

Traditional luminophores such as naphthalene diimides or porphyrins succumb to Aggregation Caused Quenching (ACQ), and so aggregation leads to quenching of luminescence of supramolecular structures containing these molecules. In molecules that show Aggregation Induced Emission (AIE), weak or no emission is observed in dissolved state; however they become luminiscent in the aggregated state or solid state. This breakthrough has metamorphosed the application of luminescent materials in organic light emitting diodes (OLEDs), and chemo- & biosensors, where the use of luminescent materials in a thin film form (solid state) or in aqueous surroundings is desirable. Tetraphenylethere (TPE) derivatives have shown most promise as AIE-active luminophores have been owing to their capability of self-organisation, and feasibility of embodiment into larger multicomponent assemblies with ACQ fluorophores. The TPE luminogen, a propeller-shaped AIE-active molecule, contains four phenyl rings around the central C=C double bond that turn emissive in solid and aggregated state due to the Restriction of the Intramolecular Rotation (abbreviated as RIR).

In this thesis, it has been shown that the functionalisation of the AIE-active luminophore TPE with four alkyl chains with either an odd or even number of carbon atoms via two amide linkages direct the morphology of superstructure by
careful control of solvent composition.

The synthesis and self-assembly of two TPE-based derivatives containing either one or two amide linkages is also described, with a flower-like self-assembly morphology observed in specific solvent mixtures, which is to our knowledge the first report on the self-assembly of flower-like 3D morphology under solvophobic control.

The effect of changing the number of carbon atoms of alkyl-TPE derivatives on the supramolecular behaviour was studied in some detail. Three new analogues of alkyl-TPE were synthesised, including seven, eight and nine carbon atoms in their long alkyl chains. Self-assembly of alkyl-TPE containing an even number of carbon atoms (i.e. eight and ten) produced various structures, whereas TPE with eight carbons formed micro-belts, and the derivative with ten carbons aggregated into flower-like superstructure. The alkyl-TPE derivative bearing an odd number of carbon atoms (i.e. seven and nine), resulted in nano-sphere superstructures.

The thesis has this extended our understanding of how the functionalisation of TPE can affect the self-assembly behaviour and morphology of the resulting superstructures, and the effect this has on AIE behaviour. To the best of the author’s knowledge, all results described here in the thesis are first reports in the scientific literature, and are thus totally novel.
Chapter 1 Introduction

Chapter-1 is a literature review on the background of AIE-active molecules.

Fig.1 Luminescent, Photo courtesy Prashant Jain
Adapted with permission from ref. 1. Copyright 2013 Nature Communication.
1.1 Literature Review

1.1.1 Supramolecular Chemistry

Supramolecular chemistry is believed to be the realm of chemistry beyond that of molecules and its focus is on the chemical systems compiled of a separate number of assembled molecular components (Figure 2). The forces responsible for the spatial organization may include weak (intermolecular forces, electrostatic or Hydrogen bonding) or strong (covalent bonding), provided that the degree of electronic coupling between the molecular component remains small with respect to relevant energy parameters of the component. While traditional chemistry focuses on the covalent bond, supramolecular chemistry examines the weaker and reversible non-covalent interactions between molecules. These forces include hydrogen bonding, metal coordination, hydrophobic forces, van der Waals forces, pi-pi interactions and electrostatic effects. Important concepts that have been demonstrated by supramolecular chemistry include molecular self-assembly, folding, molecular recognition, host-guest chemistry, mechanically-interlocked molecular architectures, and dynamic covalent chemistry. The study of non-covalent interactions has proved itself of high importance to understanding many biological processes from cell structure to vision, that depend on these forces for structure and function. Biological systems are often the trigger for supramolecular research. Supermolecules are made up of molecules, and the intermolecular interactions within the molecules.

Supramolecular chemistry in concerned with relatively weak interactions, and control over the procedures engaged is thus of utmost importance. Non-covalent bonds have low energies and usually no activation energy for formation, as indicated by Arrhenius equation, and unlike the covalent bond-forming chemistry, the rate of bond formation does not increase at higher temperatures. Chemical equilibrium dictates that the low bond energy results in a shift toward the breaking of complexes at higher temperatures.
From a historical perspective, it was Johannes Diderik Van der Waal who initially reported in 1873 the existence of intermolecular forces between molecules. Later, in 1894, Fisher suggested that enzyme substrate interactions are like a “lock and key”, which form the foundation of our modern comprehension of “Host-Guest” chemistry and molecular recognition. It was at the beginning of the 20th century that Latimer and Rodebush recounted other non-covalent interactions, namely Hydrogen bonds, which shaped our understanding of proteins and the DNA double helical structure. Later on, as chemists grasped the concepts of non-covalent interactions, they began implementing these concepts into synthetic systems. In 1960, as Pederson synthesized Crown Ethers, the research area was advanced by Cram & Lehn by synthesizing ion & shape size receptors. Supramolecular chemistry eventually gained due recognition with Cram, Lehn & Pederson’s work on host-guest chemistry receiving the Nobel Prize5.
1.1.2 Non-Covalent bonding

Fig. 3. Non-covalent interactions in biological systems. Adapted with permission from ref. 6. Copyright 2010 Essential Cell Biology (©Garland Science 2010).

The diverse non-covalent interactions which are of significance to supramolecular chemistry are outlined below:

1.1.2.1 $\pi-\pi$ Interactions

$\pi-\pi$ Interactions occur between aromatic molecules in a way that leads to the aromatic rings in such molecules being slightly polarized. The C-H bond on the periphery acquires a partial positive charge and $\pi$ electrons become partly negative charged\(^7\). Therefore, there occurs a force of attraction between the positively charged C-H bonds of one molecule with the negatively charged $\pi$- electrons on the adjacent molecule. The aromatic molecule can pile up in three different ways i.e. edge to face, face to face and
parallel displaced. These interactions are of outmost importance in RNA and DNA structure, protein folding and also in supramolecular chemistry.

1.1.2.2 Ionic interactions
Ionic interactions are described as the forces between the ions or molecules bearing full, permanent opposing charges. In an ionic bond, one atom loses the outer shell electron to form a cation which is acquired by another atom to form an anion. As a result, the cation and anion thus formed are attracted due to their opposite charges.\(^4\)

1.1.2.3 Van der Waal forces
Van der Waal interactions are the weakest amongst the non-covalent interactions. They are further subdivided into dipole-dipole, dipole-induced dipole and induced dipole-induced dipole interactions:

**Dipole-dipole interactions**
Dipole–dipole interactions are the electrostatic interaction between permanent dipoles occurring in molecules. Permanent dipoles are formed in molecules by polarisation of electrons toward the more electronegative atom.

**Dipole-induced dipole interactions**
These is the forces that can be found between the temporary dipole created in a non-polar molecule by the approach of a molecule with a permanent dipole, thereby causing the electrons in the non-polar molecule to shift towards or away from the dipole.

**Induced dipole-induced dipole interactions**
These types of force are present between all types of molecules. Induced dipoles are generated by repulsion of electrons in a molecule by electrons of a neighboring molecule, thereby causing temporary dipoles.

1.1.2.4 Hydrogen bond
Hydrogen bonding is indeed a type of dipole-dipole interaction where attraction occurs between the positive dipole of a hydrogen atom and an electronegative atom such as oxygen, nitrogen, etc. The energy needed to break a Hydrogen bond lies in the range of
0-4 kcal/mole, which is much less than a conventional covalent bond. Numerous Hydrogen bonds bestow stability for molecular interactions. The occurrence of the Hydrogen bond in a water molecule is the reason why it is liquid at room temperature rather than a gas.

1.1.2.5 Hydrophobic interactions
Hydrophobes, also known as water fearing molecules, are non-polar in nature & interact with one another, resulting in aggregation in aqueous media, excluding water molecules. These interactions serve as the backbone for the stability of protein structures. As a protein folds to hide the hydrophobic part inside & to avoid from interactions with the surrounding aqueous medium, the hydrophilic side chains, on the contrary, are exposed to the exterior side to interact with water.

1.1.3 Self-Assembly
Self-Assembly, a key concept at the core of supramolecular chemistry has been referred to “The science of things that put themselves together”. In other words, a procedure in which a disordered system of existing components forms a disciplined structure as a result of local, particular interactions among component themselves, in the absence of any external direction. When the engaged components are molecules, the process is called molecular self-assembly.
“Spontaneity” and “reversibility” are the two indivisible features of self-assembly. Organization of molecular units into ordered morphologies is led by non-covalent interactions. Spontaneity emphasizes the fact that the units get together and build the nanostructure themselves, without any exterior driving forces.
Innumerable examples occur in nature, for example biological molecules such as the DNA helix, if suitable conditions are met.
In chemical solutions, self-assembly is an outcome of the random motions of molecules and the affinity of their binding sites for one another.
1.1.4 Self-Assembly in supramolecular systems

Molecular self-assembly is a key concept in supramolecular chemistry because the assembly of molecules in such systems is conducted through noncovalent interactions (e.g., Hydrogen bonding, metal coordination, hydrophobic forces, van der Waals forces, \(\pi-\pi\) interactions, and/or electrostatic), as well as electromagnetic interactions. Widely-known examples include the formation of micelles, vesicles, liquid crystal phases, and Langmuir monolayers by surfactant molecules.\(^8\) Further examples of supramolecular assemblies demonstrate that a variety of different shapes and sizes can be obtained using molecular self-assembly.\(^9\) Molecular self-assembly allows the construction of challenging molecular topologies which are not easily made with competing technologies. One example is Borromean rings, which are interlocking rings where the removal of one ring unlocks each of the other rings.\(^10\)

1.1.5 Why study Self-Assembly?

Molecular synthesis is a technology that chemists use to make molecules through the formation of covalent bonds between atoms. By contrast, molecular self-assembly is a process in which molecules (or fragments of molecules) spontaneously form ordered aggregates and demands no human intervention; the interactions involved customarily are non-covalent. In molecular self-assembly, the molecular structure regulates the structure of the assembly\(^11\). Synthesis makes molecules; and self-assembly makes ordered entities of molecules (or ordered forms of macromolecules). The structures created in molecular self-assembly are in equilibrium.

Molecular self-assembly is omnipresent in chemistry, biology, and materials science and has been present before self-assembly emerged as a synthetic approach\(^12\&13\). The development of molecular crystals, colloids\(^14\), lipid bilayers\(^15\), phase-separated polymers\(^16\), and self-assembled monolayers\(^17\), are all instances of molecular self-assembly, as are the folding of polypeptide chains into proteins\(^18\) and the folding of nucleic acids into their functional forms\(^19\).
Self-assembly has proven itself scientifically intriguing and technologically essential for several reasons. Firstly, it plays a critical role in life. The cell encompasses a surprising range of sophisticated structures including folded proteins, lipid membranes, structured nucleic acids, protein aggregates, molecular machines, and many others that are shaped by self-assembly. Secondly, self-assembly prepares pathways to a range of materials with systematic compositions: molecular crystals and semicrystalline and phase-separated polymers are some examples. Thirdly, self-assembly materializes greatly in systems consisting of components larger than molecules, and there is a substantial prospect for its employment in materials and condensed matter science. Finally, self-assembly is one of the most common approaches for producing nanostructures. Therefore, self-assembly is relevant to a variety of subjects: physics, biology, chemistry, materials science, nanoscience, and manufacturing. There is an inspiring opportunity for self-assembly to flourish through the interchange of notions and techniques among these subjects.

1.1.6 Luminiscence

Due to the functional importance of light to human beings, a substantial amount of endeavour from the early stages of human civilization has been spent to decrypt light-emitting procedures. Emission of light by a substance not resulting from heat, i.e. cold-body radiation, is called luminescence, which is chiefly caused by chemical reactions, electrical energy, subatomic motions, or stress on a crystal. Chemiluminiscence, Bioluminescence, Electoluminescence are a few types of luminescence designated by their origin.

Aleksander Jablonski depicted the process of light absorption & emission in molecules in a diagram named after him, the Jablonski diagram. Electronic transition procedures such as light absorption, light emission, transition from singlet state to triplet states and their electron recombination at ground states through fluorescence and phosphorescence are illustrated in the diagram.
Organic luminescence has predominantly been studied in solution\textsuperscript{25,26,27,28,29}. Due to these studies, investigations have contributed profoundly to the underlying perception of luminescence procedures at a molecular level.

The light emission by luminescent material has enthralled scientists for its potential in the development of new materials and their applications & properties in several domains, namely telecommunication, optical devices\textsuperscript{30,31}, biological procedures\textsuperscript{32,33} & chemosensors\textsuperscript{34,35,36,37}. The majority of the luminescent materials have been used as thin films or in the aggregate state, for example in organic light-emitting diodes (OLEDs), which are a common optoelectronic application.

1.1.7 Aggregation-triggered luminescence

“Aggregate” is defined as “a whole formed by combining several separate elements” in the Oxford Dictionary\textsuperscript{38}. In a scientific sense, “aggregate” frequently pertains to a clump or an ensemble of components.

In the domain of luminescence studies, several organic luminophores demonstrate versatile light-emitting behaviour in dilute and concentrated solutions. It is well known that luminescence is often weakened or quenched with an increase in concentration, a phenomenon known as “concentration quenching”\textsuperscript{39}. The effect is prevalent in most
aromatic hydrocarbons and their derivatives, as outlined by Birks in his book on Photophysics of Aromatic Molecules. A chief reason for the quenching process is mechanistically linked to the “formation of aggregates” of luminophores which is probably why the concentration quenching effect has frequently been cited as “aggregation-caused quenching” (ACQ).  

![Pyrene (Emissive)](image1)

![Pyrene (Non-Emissive)](image2)

**Fig.5**  \(\pi-\pi (\pi\text{-stacking})\) Interactions, In aggregated form. Adapted with permission from ref 42. Copyright 2009 Chemical Communications.

As depicted in Fig. 2, Pyrene is an emissive molecule in solution, however as the solvent’s percentage decreases, the disk-like shapes stack up and the strong \(\pi-\pi\) interactions leads to aggregate formation with ordered or random structures. The excited state of the aggregates frequently decays through non-radiative pathways that lead to aggregation-caused quenching (ACQ) in the condensed phase.

The undesirable nature of the ACQ effect stems lies in the perspective of real-world applications. For instance, luminophores have been utilized as sensors for biological molecules in physiological buffers and also as probes to screen ionic species in river water. Although polar functional groups can be attached to a chromophoric unit to turn it into a hydrophilic unit, the resultant water-miscible luminophores are still susceptible to form aggregates in aqueous media due to the invariable hydrophobicity of their active components of \(p\)-conjugated aromatic rings. The ACQ effect is considered as a problematic barrier to the synthesis of efficient organic light-emitting diodes (OLEDs), where the luminophores are applied as thin solid films. In the solid state, the luminophore concentration reaches a maximum owing to the absence of solvent and the ACQ effect hence becomes significant.

In 2001, Tang and his group coined a novel term for the newly emerged phenomenon which functions contrary to ACQ. The studied compounds turned out to be emissive in
aggregate state, whereas their emission was turned off in solubilized state. The term aggregation induced emission (AIE) describes this desirable behaviour. Fundamental physics describes that any molecular movement (rotation, vibration, etc.) consumes energy. One prototypical AIE-gen is 1-methyl-1 2 3 4 5-pentaphenylsilole, owing to its propeller shape, an imposed Restriction of Intramolecular Rotation (RIR) unlocks radiative channels while the compound is experiencing an environment in lower percentage of solvent (ethanol) and high water content, in other words, as solvating power of ethanol/water mixture becomes poor, the nano-scopic aggregate’s clusters start to form, the propeller-shaped molecules entangled in one another and the luminescence is consequently turned on. [15].

Fig.6 Chemical Structure of AIE active propeller-shaped molecule 1-methyl-1 2 3 4 5-pentaphenylsilole. Adapted with permission from ref 49. Copyright 2016 Chemical Education.

Non-emissive                                                                                               Emissive

In a nutshell, 1-methyl-1 2 3 4 5-pentaphenylsilole is non-emissive when its molecules are dissolved in a good solvent, such as ethanol or an ethanol/water mixture with a fraction of water ($f_w$) lower than 80 vol%. In this environment, the five phenyl peripheries in 1-methyl-1 2 3 4 5-pentaphenylsilole can actively rotate against the silole core (Figure 6). However, its fluorescence is turned on when $f_w$ reaches ca. 80 vol%. It becomes strongly fluorescent at $f_w = 90$ vol%, thanks to the substantial aggregation of this molecules in aqueous medium with poor solvating power. In the AIE system, the aggregates (the whole) are more luminiscent than the individual molecules whereas in the ACQ system the contrary is correct; the individual components luminesce better than the aggregated structrue. Generally speaking, the AIE effect originates from the restriction of intramolecular motion (RIM), which includes restriction of intramolecular rotation (RIR) and restriction of intramolecular vibration (RIV) [51].
To further explain typical ACQ & AIE phenomena, Figure 7 (A) illustrates the gradual decrease in fluorescence of 1,4-di[(E)-styryl]benzene as water fraction increases and solvent’s percentage decreases. Since the organic molecules are not highly soluble in water, however, by changing the water fraction the planar compound tends to form aggregates which consequently quench the emission.

Strong $\pi$–$\pi$ stacking interactions are observed in the face-to-face packing structure, which facilitates excimer formation, leading to weakening light emission which is visually discernible.

On the other hand, the $\alpha$-dimethylated derivative of the same compound, because of the steric obstruction of the two methyl groups, clings to a non-planar conformation acquired through out of the central plane twisted C-C double bonds. The intramolecular interaction is weakened by this twisted geometry and the probability of excimer formation in the crystal diminishes. This restriction of intramolecular rotations (RIR) is again at work to lock the irradiative channels & to open up the radiative routes. It is concluded that the molecules become emissive in the aggregate state. Thus, RIR has been considered to be the reason behind aggregation induced emission. Evidently, the photoluminescence (PL) behaviour in (B) is typical of an AIE

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**Fig.7** (A) Molecular packing arrangements & emission behaviour of 1,4-di[(E)-styryl]benzene (B) and its $\alpha$-dimethylated derivative. Adapted with permission from ref 41. Copyright 2011 Chemical Society Reviews.
Luminogen. In the solution phase, this non-planar molecule is indeed non-emissive due to the minuscule bonding on the building blocks that allow active intramolecular rotation, that impedes its excitons and this eventually results in no emission.

Since organic luminescence is chiefly dominated by electronic conjugation, a favoured structural design strategy has been to expand the scope of p-conjugation using aromatic rings. The resulting larger discotic plates can consequently luminesce more efficiently in solution, but simultaneously their ACQ effects grow because the prospects for such large luminophores to create excimers are also increased.

1.1.8 Tetraphenylenethylene as an AIE-gen

1.1.8.1 Structure
Tetraphenylethene (TPE) is a well-studied AIEgen, in which four phenyl rings are linked to a central ethene rod through single bonds (Figure 8). The phenyl rings have considerable freedom to rotate around the ethene linker. Isolated molecules of TPE in a dilute solution can experience active intramolecular rotations, which works as a relaxation pathway for the excited states to non-radiatively decay to the ground state. In the aggregated state, these intramolecular rotations are confined, which hinders the irradiative relaxation routes. The above analysis implies that the RIR process is responsible for the AIE phenomena of molecular rotor systems.

Fig.8 Propeller-shaped tetraphenylenethylene (TPE) is non-emissive in a dilute solution but becomes emissive due to the restriction of intramolecular rotation (RIR) in the aggregate state. Adapted with permission from ref 51. Copyright 2014 Advanced Materials.
1.1.8.2 Applications

Amongst aromatic molecules that have found efficacy, especially for mechanochromic luminescent materials, tetraphenylethylene (TPE) molecules have gained a great deal of attention because of their inclination towards being non-emissive in the dissolved state, but increased emission in both the aggregated form and the solid state. Since then, TPE derivatives have been used for supramolecular building blocks, fluorescence “turn on” chemosensors for selective detection of Ag$^+$ and Hg$^{2+}$ ions and acid/base sensing in solution and living cells.

In order to design fluorogens for biological applications to detect & screen a biological process or biological agents, the probe behaviour has to be investigated precisely beforehand.

Despite the fact that some luminogenic molecules can be used in their solubilised state when the pH or a small ion is to be screened, a single luminescence signal is generally needed when the probe is related to a target analyte, either aggregated or in a self-assembled state. Most of the probes do not turn out to be successful due to the ACQ effect, however molecules that form aggregates open up another route for the excited molecules relaxation, resulting in quenching the fluorescent emission.

TPE derivatives that display AIE behaviour provide a solution to engineer novel bioprobe molecules. Taking advantage of this characteristic, several researchers have utilized TPE derivatives for biological applications such as bioprobes, Finger Print Identification, chemosensors, and cell imaging, cell labelling, etc.

Figures 9 & 10 illustrate a few of the wide-spread applications of TPE-derivatives.
The photo-physical properties and self-assembling ability of the TPE core can also be used for sensing small ions. For example, a selective Cu (II) detector was developed using AIE active TPE macro-cycle nano-fibers\(^{60}\) (Figure 11).

While copper ions are non-existent, a colour change from colourless to yellow colour was recorded. An extreme change of colour occurs accompanied with changes in the UV–Vis spectrum by copper ions addition, with a Cu (II) concentration even as low as 1.0×10\(^{-5}\) M detectable. This enables analysis copper ions to see if they exceed the standard safe level in drinking water, (2.0×10\(^{-5}\) M according to the Environmental Protection Agency (EPA)). Intriguingly, no apparent alteration was observed in the UV–Vis spectra when other metal ions, namely Fe\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\), Zn\(^{2+}\), Cd\(^{2+}\), Hg\(^{2+}\), Mn\(^{2+}\), Ag\(^{+}\), Cr\(^{3+}\), Pb\(^{2+}\), Al\(^{3+}\), Ca\(^{2+}\), Mg\(^{2+}\), K\(^{+}\) and Na\(^{+}\), were added to the solution, as shown in Figure 12.
These results demonstrate that aggregated TPE macro-cycle nano-fibers are a favourable candidate for sensitive and selective screening of copper ions in drinking water.
Fig. 13 (I) Photos of TPE-derivative applied as Cu (II) detector (Fig. 11) in H2O–THF 2[thin space (1/6-em)]:[thin space (1/6-em)]1 under daylight and (II) photos of 3 in H2O–THF 9[thin space (1/6-em)]:[thin space (1/6-em)]1 under 365 nm light after addition of the metal ion ([3] = 1.0 × 10−5 M, [metal] = 2.0 × 10−5 M). Adapted with permission from ref 60. Copy Right 2014 Materials Chemistry B.

1.1.9. Responsive Smart Materials

The majority of AIEgens are described as “smart” or “intelligent” materials, whose luminescence properties change in response to exterior stimuli or environmental alternations, namely electric field, mechanical force, fuming (vaporising), temperature alternations, pH (in medium range), photonic irradiation, solvent polarity or storage time. The luminescence alteration with mechanical force is a chromic effect widely noticed in many AIE systems. Mechanochromic materials of this type have substantial potential application in fields such as pressure sensors, information storage, and security inks. The mechanochromic effects of the AIEgens are frequently coupled with changes in their molecular packing structures. A propeller shape with a highly twisted conformation is indeed one of the most well-defined structural characteristics of an AIEgen. The untied packing morphology of such propeller-shaped AIE molecules is responsive to exterior agitation; leading to an increase in the chromic response. A prototypical mechanochromic AIEgen, BTPE-FN (2,3-bis(4′-(1,2,2-triphenylethenyl)biphenyl-4-yl)fumaronitrile), is depicted in (Fig. 14). After grinding, the emission color changes from yellow to orange. Upon thermal treatment at 160ºC or vapor fuming by dichloromethane, the emission color is regressed. Mechanistic studies unveil that the mechanochromism is linked to morphological transformation between crystalline and amorphous states.

Light emission of almost all AIEgens of a defect-sensitive nature decrease after being mechanically ground.
Fig.14 (a) Structure of BTPE-FN. (b) Solid-state emissions of BTPE-FN: fluorescence photographs of (I) as-prepared sample and the samples after (II) mechanical grinding, (III) thermal annealing and (IV) solvent fuming. (c) Writing-erasing processes realized through utilization of BTPE-FN. Adapted with permission form ref. 70. Copy Right 2013 Physical Chemistry.

1.1.10 Odd & even self-assembly

In this thesis, molecules contain chains with an odd and even number of Carbon units are studied to probe how the odd-even effect can be used to engineer the morphology of self-assembled structures. The odd-even effect on structure and properties is a commonly observed phenomenon in chemistry, physics, biology, and materials science. Generally speaking, it depicts an alternative change in a materials structure and/or properties depending on whether there are an odd or even number of structural units in a molecule. The structural unit could include one CH2 group (such as in this thesis), one metal atom, or another more sophisticated unit. It occurs in macroscale materials such as in the boiling points of liquid n-alcohols. Moreover, it is broadly recorded at several organic/solid surfaces and interfaces. Surface and interfacial interactions are a central point for the development of heterogeneous materials, for
example heterogeneous catalysts and various functional organic thin films, and for the
design of nano-devices and biosensors.

Interactions at the surface and interface can be categorized as weak non-covalent
interactions and strong chemical-bond interactions. Recent systematic studies have
shown that organic thin films can be formed through these two distinctly different
interfacial interactions at the organic/solid interface\textsuperscript{73,74,75}.

The driving forces for the odd-even difference in the self-assembled structure are
generally associated with intermolecular hydrogen bonds. Figure 15 illustrates the
difference in the hydrogen bonding of the two structures. The -OH terminations of HO
(CH\textsubscript{2})\textsubscript{n-1}COOH\textsubscript{n} (even) are in a favourable orientation to form an H-O, H-O hydrogen
bond with the neighbouring molecules. However, for the molecules with an odd
number of carbon atoms, the added CH\textsubscript{2} group attached to the terminal OH creates an
undesired conformation in which the OH group cannot form a hydrogen bond with the
OH group of its adjoining molecules. In a nutshell, the odd or even length of the
middle chain, the alkyl spacer (CH\textsubscript{2})\textsubscript{n}, dictates the extension directions of the two side
functional groups\textsuperscript{76}.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure15.png}
\caption{Molecules with an even number of CH\textsubscript{2} units between two C=O groups
can form two intermolecular hydrogen bonds between molecular chains at the head
moiety and terminal moiety. Molecules with an odd number of CH\textsubscript{2} groups between
two C=O groups only form one intermolecular hydrogen bond at the head moiety.
Adapted with permission from ref. 76, Copyright 2007, Chemical Reviews.}
\end{figure}

In amides, linear hydrogen bonds are feasible only in the case of the even homologues,
because two similarly distant CO-NH pairs occur on each edge of the chain. In the
odd-numbered amides, both N-H groups and both C=O groups are located on a single
edge and the distances are not the same. Linear hydrogen bonds cannot be formed. The
odd homologues should be unstable because only one chain of linear hydrogen bonds is achievable.

1.2 Literature limitations and project aims

The ever-developing AIE (Aggregation Induced Emission) field originates from its promise as an emerging and effective solution to tackle the problems caused in real applications from ACQ (Aggregation Caused Quenching).

Within the scope of this thesis, the literature review describes the background knowledge of the core subject, starting with the basics of supramolecular chemistry and self-assembly, the essence of AIEgen properties and features, and the archetypical AIEgen, TPE (Tetraphenylenethylene) and its derivatives are further introduced, with their applications are briefly mentioned.

With this in mind, in this thesis the synthesis of amphiphilic and dumbbell shaped AIE-active tetraphenylenethylene (TPE) derivatives have been studied & their self-assembly with solvophobic control has been scrutinized. Two TPE derivatives form a 3D flower-shape supramolecular structure from THF/water solutions at varying water fractions. SEM microscopy was used to visualize the gradual growth of the flower-shape assembly. These TPE derivative self-assemblies are formed due to two main important properties: (i) the TPE-core along with alkyl chains, optimizing the dispersive interactions within a construct, and (ii) amide-linkage through molecular recognition.

Furthermore, 4 TPE-derivatives with an odd and even number of carbons in their chain have been synthesized and their self-assembly morphology investigated.

Here in this thesis, the applications of TPE luminogens have been described as:

I. Superstructure of TPE luminogens through solvophobic controlled self-assembly
II. Odd-even effect on Supramolecular Nanoarchitecture via self-assembly

1.3 Aims of this Master’s project

Following the literature review and significant role of TPE-derivatives as a distinctive AIEgen, this master’s project will aim to design and develop novel materials that will
study the functionality of the TPE- derivatives’, in order to better understand synthetic methodology & subsequent controlled assembly.

The main focus of this master work will be the design of novel materials in such a way that they succeed in the fundamental structural requirements: namely solubility, stability, and aggregation induced emission with high quantum yields. We will them consider design prerequisites that will assist us to synthesize target TPE-derivatives for supramolecular chemistry-related purposes.

1.4 Outline of Master’s thesis chapters

This thesis is written as a thesis by publication. The detailed description of published journal articles is as follows:

Chapter 1 - Introduction and literature review
This chapter discusses the background knowledge of the core subjects in the thesis.

Chapter 2 - Consists of published paper by Nature Publishing Group (Scientific Reports)
Flower-like superstructures of AIE-active tetraphenylethylene through solvophobic controlled self-assembly, Mina Salimimarand, Duong Duc La, Mohammad Al Kobaisi and Sheshanath V. Bhosale (Scientific Reports 7, Article number: 42898 (2017) doi: 10.1038/srep42898)

Chapter 3 - Consists of to be published paper by Applied Sciences
Influence of Odd and Even Alkyl Chains on 2 Supramolecular Nanoarchitecture via Self-Assembly 3 of Tetraphenylethylene based AIEgens, Mina Salimimarand, La Duong Duc La, Sidhanath V. Bhosale, Lathe A. Jones, Sheshanath V. Bhosale (Appl. Sci. 2017, 7(11), 1119; doi:10.3390/app7111119)

Chapter 4 - Conclusion and future work
This chapter describes an overview of the thesis work and future directions.
1.5 References


Wang H., Zhao E., Lam W.Y., Tang B.Z., AIE luminogens: emission brightened by aggregation, J.mattod.2015.03.004.


Chapter 2 Scientific Reports

**Chapter 2** – describes “Flower-like superstructures of AIE-active tetraphenylethylene through solvophobic controlled self-assembly”, from the published paper in Scientific Reports, 2017, doi:10.1038/srep42898
Flower-like superstructures of AIE-active tetraphenylethylene through solvophobic controlled self-assembly

Mina Salimimanand, Duong Duc La, Mohammad Al Kobaisi & Sheshanath V. Bhosale

The development of well-organized structures with high luminescent properties in the solid and aggregated states is of both scientific and technological interest due to their applications in nanotechnology. In this paper, we described the synthesis of amphiphilic and dumbbell shaped AIE-active tetraphenylethylene (TPE) derivatives and studied their self-assembly with solvophobic control. Interestingly, both TPE derivatives form a 3D flower-shape supramolecular structure from THF/water solutions at varying water fractions. SEM microscopy was used to visualise step-wise growth of flower-shape assembly. TPE derivatives also show good mechanochromic properties which can be observed in the process of grinding, fuming and heating. These TPE derivative self-assemblies are formed due to two main important properties: (i) the TPE-core along with alkyl chains, driving the dispersive interactions within a construct, and (ii) amide-linkage through molecular recognition. We believe such arrangements prevent crystallization and favour the directional growth of flower-shape nanostructures in a 3D fashion.

Supramolecular self-assemblies of small aromatic organic π-conjugated molecules have attracted enormous attention of researchers due to their applicability in optoelectronics, chemosensors, nanotechnology, biotechnology and biomedicine. Where non-covalent interactions (hydrogen-bonding, π-π interaction, van der Waals forces and electrostatic attraction) play important roles in the creation of controlled 1, 2 and 3 dimensional superstructures, such as nanowires, nanotubes, nanoribbons, nanobelts, nanosheets, spheres, capsules, and nano/micro-flowers from small aromatic π-conjugated functional molecules.

The massive morphological changes of supramolecular assemblies have been widely investigated, however, flower-like assemblies of small organic molecules are rare. During the past decade, flower-shaped inorganic/organic assemblies gained the attention of researchers due to their potential applications in the various fields such as catalysis, superhydrophobic, explosives detection, magnetic materials, biomedical and optoelectronic materials. In this regards, Nakanishi and co-workers reported the formation of organic flower-shaped morphology via self-organization of functionalised C60 derivative. Furthermore, few examples for the construction of organic flower-like nanostructures from diphenylalanine dipeptide and DNA also reported. Very recently, we reported flower-like structures assemblies of naphthalene diimide appended phosphonic acid with melamine from aqueous medium through strong hydrogen-bonding and electrostatic interaction.

However, these assemblies suffer from drawbacks where aggregation caused quenching (ACQ) was observed, which is encountered in most conventional fluorophores used to form these assemblies. ACQ occurs due to the formation of excimers through π-π stacking of fluorescent molecules providing non-radiative relaxation pathways of the excited states. Secondly, the organic flower-shaped morphology field is in its infancy and has not been explored with respect to AIE-active small organic molecules.

To further explore this idea, tetraphenylethylene (TPE) was used due to its aggregation induced emission (AIE) properties, contrary to the ACQ-effect of most commonly used small molecules in flower assembly. It is a non-planar, propeller shaped molecule, which is easily prepared with excellent yield. The AIE-effect mechanism is explained by the restriction of the intramolecular rotations (RIR) which restrict the non-radiative relaxation of the molecules via mechanical and thermal pathways, hence making the electronic emissive relaxation the

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preferred, highly probable pathway\textsuperscript{30}, TPE, in particular, is utilized in designing mechanoluminescent materials, due to its capability of self-organisation and the ability to be incorporated into larger supramolecular assemblies via solvophobic control\textsuperscript{45}. TPE luminophores are widely used in various fields such as organic, biological, supramolecular, electronic, and medicinal chemistry\textsuperscript{41}. TPE applications include chemical sensors, optoelectronic devices, organic solar cells, light emitting diodes and field effect transistors\textsuperscript{41-42}. There has been various chemical, physical, and molecular design approaches used to synthesise TPE luminophores, whose absorption and emission properties can be tuned to optimize their solubility in polar and non-polar solvents. For example, the attachment of bulky aldehydes, encapsulation in amphiphilic molecules, and blending with polymers etc.\textsuperscript{43}. Although TPE is widely used in various fields, however, designing small organic molecules with the potential of producing well-organised supramolecular nanotechnology with efficient luminescence in solid states is still rare.

Results

We recently became interested in the design and development of novel AIE-active TPE luminogens with supramolecular self-assembly potential to produce variety of nanostructures such as star shaped\textsuperscript{44}, controlled helical\textsuperscript{45}, highly efficient near-IR solid emitter\textsuperscript{45}, metal organic framework\textsuperscript{46}, and use in various applications such as sensing of organic volatiles\textsuperscript{47}, pH sensor\textsuperscript{48}, bioimaging\textsuperscript{49}, and donor-acceptor systems for solar cells\textsuperscript{50}. As part of our on-going program, we investigated the synthesis of dumbbell-shape TPE-1 and TPE-2 amphiphilic molecules (Fig. 1).

Both TPE-1 and TPE-2 compounds were synthesized by amide coupling of amino-TPE and alkyl-dicarboxylic acid and alkyl-carboxylic acid in the presence of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDCI) and 4-dimethylaminopyridine (DMAP) in dry DMF; the synthetic procedure shown in Scheme 1 (for details see ES1). Both compounds were characterized using H\textsubscript{1}, C NMR, IRMS and elemental analysis. TPE-1 and TPE-2 are highly soluble in common organic solvents such as THF, chloroform, dichloromethane (DCM) and insoluble in acetonitrile, methanol, water and hexane.

Figure 2 shows luminescence properties of TPE-1 and TPE-2 through solvophobic control. Compound TPE-1 produces a faint emission in solution, while produces strong fluorescence in its aggregated state in THF/water and CHCl\textsubscript{3}/hexane, however, no FL was observed in THF/MeOH and THF/ACN. Interestingly, TPE-2 only emits strong fluorescence in the aggregate state in THF/water. Here we use TPE as an extended \( \pi \)-conjugated moiety, amide group for a hydrogen-bonding and the alkyl chain as a segment that can introduce van der Waals interaction to the self-assembly process.

UV-vis absorption and fluorescence spectroscopy. The photophysical properties of TPE-1 and TPE-2 were screened using UV-vis absorption and fluorescence spectroscopy in polar and mixture of polar and non-polar solvents as shown in Fig. 3. The UV-vis absorption spectrum of both TPE-1 and TPE-2 derivatives in THF (1 \( \times \) 10\textsuperscript{-3} M) exhibited \( \pi \)-\( \pi \) transition with absorption maxima at 325 and 260 nm (Fig. 3a). The photoluminescent (PL) spectrum of TPE-1 in THF shows no detectable signals (Fig. 3b,c). Furthermore, the solvatochromic properties of TPE-1 and TPE-2 were surveyed at various water fractions (\( f_w \)). No spectral changes were observed upon the increase of water fractions between 10 and 50% \( v \) in THF/water solvent mixture. Both luminogens become emissive when water fraction increases to \( f_w = 65-80\% \) \( v \), where PL spectra show a red-shift of 15 nm and an enhanced emission of 25-fold at 475 nm due to molecular self-assembly. This is a clear verification of the AIE characteristics of TPE-1 aggregates, owing to decreased solubility with increasing \( f_w \) in THF. Interestingly, at addition of 99% water fractions, the FL intensity enhanced rapidly, and the luminescence maxima split to two peaks one blue-shifted to 418 nm and the other red-shifted to 505 nm. Further increase of \( f_w \) to 95% \( v \) shifted the two luminescence maxima to 425 and 535 nm, respectively. As \( f_w = 95\% \) \( v \), a 70-fold enhancement of emission has been observed as compared to that in 100% THF. Similar phenomenon was also observed for TPE-2 as shown in Figs 3d and S1. The fluorescence quantum yield (\( \Phi_F \)) of TPE-1 and TPE-2 in 100% THF solutions are 0.05 and 0.09% which were enhanced by 70-fold to 3.61 and 6.78% at \( f_w = 95\% \) \( v \) respectively, as measured with Rhodamine B as a standard with \( \Phi_F = 70\% \) in ethanol.
Figure 2. Luminescence properties: photographic images of TPE-1 and TPE-2 solutions in various solvent mixtures irradiated by UV light (λe = 365 nm).

Figure 3. Solution based self-assembly. (A) The UV-vis absorption spectra of TPE-1 and TPE-2 (10μM), (B) the fluorescence spectra of TPE-1 (10μM) in THF/water at various water fractions, (C) and (D) fluorescence intensity changes of TPE-2 and TPE-1 at 475 nm as a function of water fraction in THF solvent mixture and irradiation at 365 nm, respectively.
Density functional theory. Density functional theory (DFT) calculations with Gaussian 09 suite of programs and B3LYP/6-311G level of theory was used to optimize molecular conformation of TPE-1 and TPE-2 in the gas phase and calculate the HOMO–LUMO gap. The similarity of the spectroscopic properties of TPE-1 and TPE-2 is due to the similarity of the electronic structure of these two compounds. The symmetry in TPE-1 results in the degeneracy of the electronic states producing two states per energy level. The HOMO–LUMO gap of TPE-1 and 2 are 309.6 nm (4.003 eV) and 308.4 nm (4.020 eV) respectively. Similarly, the HOMO-1 to LUMO transition for TPE-1 and TPE-2 required 248.2 nm (4.995 eV) and 248.1 nm (4.997 eV) wavelength respectively. These are very close values due to the electronic structure of chromophores in these two molecules. The distribution of electron density of the HOMO and LUMO orbitals of TPE-1 and TPE-2 show similar distributions as shown in Fig. 4.

Field Emission Scanning Electron Microscopy. The dumbbell shaped TPE-1 produced nano-sphere particle about 80-140 nm in diameter when deposited from a solution with \( f_0 = 85\% \) in water-THF solvent mixture (Fig. 5C). These particles tend to aggregate at \( f_0 = 95\% \) forming a network of fused particles (Fig. 5D). These particles nucleate in the solution due to lower solubility of TPE-1 in high \( f_0 \), with no surface initiated self-assembly occurs during solvent evaporation on the substrate at these high \( f_0 \). At lower \( f_0 \), of 90\% we observe an increased TPE-1 solubility of and thus a combination of nanoparticles and ribbons and ribbon aggregates, which form upon solvent evaporation (Fig. 5B). The solubility of TPE-1 increases further at \( f_0 = 70\% \), the self-assemblies formed from this solution are flower-like fractal microstructures composed of short ribbons grown radially from one centre on the substrate surface. This can be justified by the coexistence of oligomer aggregates and molecular TPE-1 in solution, where the solubilized molecules produce surface initiated self-assemblies during solvent evaporation (Fig. 5A).

TPE-2 produced aggregated ribbons at \( f_0 = 70 \) and 80% (Fig. 5E, F). Fractal flowerlike structures were produced at \( f_0 = 85\% \) (Fig. 5C). These microstructures are single centred, half spherical, fractals composed of crystalline nanosheets about 120 nm in thickness and 0.5–1.0 μm in width (Fig. 5G inset). This fractal structure initially grows radially on the substrate surface, and at later growth stages fill a 3D half sphere, giving a fractal flower-like structure. Increasing water fractions to 95%, TPE-2 produced irregular sheets deposition (Fig. 5H).

The TPE-2 fractal self-assemblies showed a defined crystallinity as evidenced by the defined X-ray diffraction (XRD) pattern (See Figure S2)59. This crystallinity arises from the ribbons composing the fractal structures, which may be induced by the crystallinity of silicon wafer surface, directing the self-assembly of the initial layer in a preferred orientation resulting in crystalline growth in a specific plane.

Direct visualisation of the Self-assembled microstructures using SEM provides unique insight in the mechanism of flower assembly. Figure 6 clearly shows the step-wise growth mechanism of 3D flower like fractals of TPE-2 in water-THF \( (f_0 = 85\%) \). The samples were prepared by solvent evaporation over 3 hours and the SEM images
Figure 5. Visualisation of various self-assemblies by SEM analysis. SEM micrographs of microstructures of TPE-1 from solutions in (A) $f_1 = 70\%$, (B) $f_1 = 80\%$, (C) $f_1 = 85\%$, (D) $f_2 = 95\%$, and TPE-2 deposited from solutions in (E) $f_1 = 70\%$, (F) $f_1 = 80\%$, (G) $f_1 = 85\%$, (H) $f_2 = 95\%$ of water-THF solvent mixtures.

Figure 6. Flower-like assembly formation process. SEM micrographs of TPE-2 deposited by solvent evaporation of water-THF ($f_1 = 85\%$) solutions, showing a step-by-step growth of the flower-like 3D fractal microstructure (The scale bar indicates 10 μm).
Figure 7. The mechanochromic properties. TPE-1 (A–D) and TPE-2 (E–H) showing the luminescence of these two compounds after grinding, fuming and heating. The fluorescence spectra of (I) TPE-1, and (J) TPE-2 at the powder crystalline, ground, fumed and heated states, respectively.

Mechanochromic properties. Both TPE-1 and TPE-2 show mechanochromic properties which can be observed in the process of grinding, fuming and heating, respectively as shown in Fig. 7. The luminescence properties of such compounds are subject to the molecular packing in the solid state. This is in agreement with AIE behaviour of TPE-1 and TPE-2 in solution, where the stacking of the TPE moieties in self-assembly hinders non-radiative relaxation pathways, the same can occur in the crystalline solid state. Grinding TPE-1 and TPE-2 gave powders with the same emission colour, which is an evidence of retaining the crystalline structure in the process. The reduction in the intensity of the ground material is due to the reduction in the crystallite size distribution. Fuming the ground materials reverted them to their initial luminescent states in colour and intensity. Heating the grounds at 100 °C for 3 min has reduced the luminescence in both TPE-1 and TPE-2 (Fig. 7D,H).

The solid state fluorescence spectra of TPE-1 and TPE-2 at various stages show a similar trend to the spectra at various f, in solution, where various aggregate sizes are produced (Fig. 7I,J). TPE-1 initial powder, as shown in the SEM images, is composed of nanospheres with very fine particle size, and therefore giving weak luminescence at 477 nm. Grinding this material fused some particles increasing the particle size distribution and enhanced the fluorescence intensity. Furthermore, fuming the ground material increased crystallites size and further enhanced luminescence intensity with a blue shift to 470 nm. Heating the fumed material gives an amorphous material with less restriction on the non-radiative relaxation pathway and resulting in significant decrease in luminescence intensity. As we have seen in solution, TPE-2 shows a different luminescence behaviour in comparison to TPE-1. The initial powder of TPE-2 is well crystalline material which gives two peaks at 407 and 498 nm. Grindng this material changes the fluorescence pattern to a single broad peak around 450 nm. After fuming the ground TPE-2,
the spectrum reverted to two peaks at 425 and 485 nm with a red shift in the first and blue shift in the second bands. Heating the fumed powder reduces luminescence and reverts the luminescence spectrum of two peaks pattern to a single peak at 448 nm. This shows the strong sensitivity of TPE-1 and TPE-2 molecular stacking in the crystal structure to thermal and mechanical forces, where heating can allow the non-radiative relaxation pathways due to formation of amorphous material with reduced luminescence.

The AIE behaviour of TPE-1 in chloroform-hexane solvent mixtures is similar to trend seen for this compound in THF-water (Fig. 8A). The better solubility of TPE-1 in organic solvents in comparison to THF-water has shifted the AIE in solution to high ratios of hexane ≥95% v. The self-assembly of TPE-1 when deposited from f_0 = 95% v in chloroform-hexane on a silicon wafer, shows flower like microstructure as well as nanoparticles. The two centres of the fractal are positioned between two lobes and 4–5 μm apart (Fig. 8B). The flower like microstructures are two lobed with dual centred fractal growth and 20–30 μm in diameter, composed of sheets few tens of nanometers in thickness.

This work demonstrates that complex self-assembly can indeed be attained through hierarchical non-covalent interactions i.e. hydrogen-bonding, π–π interaction and van der Waals forces through solvophobic control. Figure 9 illustrates a schematic arrangement of TPE-1 CHCl₃/hexane (f_0 = 95%) and TPE-2 in THF/water (f_0 = 85%) to form stacks which can further hierarchically assemble to form the larger flower like structures due to the solvophobic interactions and H-bonding.

**Discussion**

The formation of micrometer-sized flower-like supramolecular structures was obtained by hierarchical self-assembly of a tetraphenylethene (TPE) derivatives in aqueous–organic solvent mixture medium for the first time. It can be noted that the flower-like microstructures several micrometers in size (10–30 μm) are composed of flake-like nanostructures several nanometers in thickness. The solution of TPE-1 in CHCl₃/hexane (f_0 = 95%) and TPE-2 in THF/water (f_0 = 85%) were aged for at least three hours and then evaporated to allow for subsequently air drying on a silicon wafer substrate, this has left flower-like superstructure on the substrate surface. The formation of such flower-like fractal assembly is attributed to a balance between the intermolecular interactions, including the π–π interaction that require a perfect stacking alignment and H-bonding and van der Waals interactions that require a torsion adjustment angle to relieve the hindrance in the self-assembly which results in a smaller intermolecular torsion angle. This allows molecules to form supramolecular assemblies in a controlled
3D fashion as illustrated in Fig. 9. Similar to many other TPE derivatives, TPE-1 and TPE-2 show AIE behavior in aggregated state that can form in a bad solvent media such as high water fraction mixtures with organic solvents. Interestingly, TPE-2 in THF/water (f_w = 85%) self-assembled into flower-like structures. However, TPE-1 assembled into spheres in similar water contents and dual centred two lobe surface initiated fractal growth in CHCl_3/hexane upon solvent evaporation.

The SEM analysis importantly shows the ability to build microstructures based on self-organization using solvophobic effect and molecular noncovalent interactions into well-defined and discrete complex morphologies such as flower-like objects. This may inspire further advances molecular superstructural design based on self-assembly theory that go beyond simple morphologies. To the best of our knowledge, the flower-shaped morphology forming from an AIE-active molecule to the supramolecular described herein is the first example of such assembly being observed in a supramolecular system containing single molecule. The results described in this paper demonstrate an actionable roadmap to about how to handle intermolecular interaction in molecular design and utilizing the solvophobic effects and thermal and mechanical stimuli which can guide further advances in supramolecular geometrical design and functionality. Furthermore, flower-like structures of AIE-active molecule built using solvophobic control indicate their potential application in various fields in combination with other chemical entities.

Materials and Methods
TPE, chloroform (CHCl_3), chloroform-d (CDCl_3), methanol (MeOH), dichloromethane (DCM), Tetrahydrofuran (THF), N,N'-dimethylformamide (DMF) were purchased from Aldrich and used without purification, unless otherwise specified. Fluorescence measurements were performed on a FluoroMax-4, Horiba Jobin Yvon, equipped with an injector port, a stirrer and a temperature controller (25°C). 1H NMR, 13C-NMR spectra were recorded on a Bruker spectrometer using CDCl_3 and MeOD as solvent and tetramethylsilane as an internal standard. The solvents for spectroscopic studies were of spectroscopic grade and used as received. Mass spectra (MS) were obtained by using Bruker AutoFlex Matrix Assisted Laser Desorption/Ionization (MALDI) Time of Flight (TOF)-Mass Spectrometer (MALDI-TOF-MS). The X-ray diffraction (XRD) pattern spectra were performed on a Bruker D8 FOCUS diffractometer using a Cu target radiation source (λ = 0.15418 nm).

Spectroscopic measurements. UV-Vis measurements. UV-Vis absorption spectra were recorded in a Cary-50, and UV-Vis spectrometer in 1 cm path length cuvette. A 0.2 mL aliquot of the stock solution of TPE
Fluorescence Measurements. Fluorescence emission spectra were recorded in a Horiba Jobin Yvon Fluoromax-4 Spectrofluorometer. Fluorescence measurements and quenching experiments were performed on a Fluoromax-4 equipped with an injection port and stirrer at 25°C. All experiments were performed in a quartz cell with a 1 cm path length with 365 nm excitation wavelength.

SEM imaging. The silicon wafer was cleaned by acetone, ethanol and then Milli-Q water. SEM samples were prepared by sonication evaporation on a silicon wafer and then sputter coated with gold for 10 s at 0.016 mA Ar plasma (SPI, West Chester, USA) for SEM imaging using a FEI Nova NanoSEM (Hillsboro, USA) operating at high vacuum which provided direct visualisation of the self-assembled aggregated structures.

Transmission Electron Microscopy (TEM) imaging. TEM samples were prepared by sonication evaporation on a holey carbon grid and thinnegatives were prepared using a Leica 1010 RE TEM.

Fourier Transform Infrared Spectroscopy (FTIR). FTIR spectra were collected on a Perkin Elmer FT-IR 400 at ambient temperature. The instrument was continuously purged with CO$_2$-free dry air.

Quantum efficiency ($\Phi_q$). The fluorescence quantum efficiency ($\Phi_q$) of the samples with absorption (intensity $\sim 0.05$) was estimated using fluorescein in ethanol ($\Phi_q = 0.95$) as standard solution and $\Phi_q$ of the solid films was measured using an integrating-sphere photometer.

Molecular modeling. Density functional theory (DFT) calculations with no consideration of dispersion interactions in gas phase were conducted using Gaussian 09 suite of programs.

References

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Author Contributions
M.S. performed syntheses and structure determination along with UV-vis and fluorescence spectroscopy. D.D.L. and M.A.X. performed surface based assembly to visualize the flower structures by SEM, TEM and also have performed XRD analysis. S.V.R. (RMIT) directed the research, interpreted and analyse the data and wrote the full manuscript. All co-authors reviewed the manuscript.

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Supplementary Information

Flower-like superstructures of AIE-active tetr phenylethylene through solvophobic controlled self-assembly

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Fig. S1 Fluorescence spectra of TPE-2 (10 μM) in THF/water at various water fractions.
Fig. S2 Powder XRD of TPE-2 deposited in the $f_w$ of 85% to produce flower like fractals (blue), 80% to produce nanosphere (black) self-assemblies and ground material (red).

Fig. S3 TPE-2 deposited from $f_w = 70\%$ in THF-water mixture.
Fig. S4 TPE-2 deposited from $f_w = 80\%$ in THF-water mixture.

Fig. S5 TPE-2 deposited from $f_w = 85\%$ in THF-water mixture.
**Fig. S6** TPE-1 deposited from $f_w = 70\%$ in THF-water mixture.

**Fig. S7** Optical images (Fig. A and B) and SEM images (Fig. C and D) of TPE-2 deposited on silicon wafer by solvent evaporation of water-THF($f_w = 85\%$) solutions.
**Fig. S8** Optical images of TPE-2 deposited on silicon wafer with water-THF ($f_w = 85\%$) solutions after taking in-situ microscopy imaging.

**Fig. S9** TEM micrographs of microstructures of TPE-1 and TPE-2: a & c) TPE-1 deposited from $f_w = 80$ and $85\%$ % from THF-water mixture. b) TPE-1 from $f_w = 95\%$, and d) TPE-2 deposited from $f_w = 85\%$ in THF-water mixture.
Synthesis of TPE derivatives


Synthesis of TPE-1: Sebacic acid (0.1 g, 0.5 mmol) and amino-TPE (0.407 g, 1.08 mmol) added to DMF (8 ml) at 0 °C and stirred for 10 min under nitrogen atmosphere, followed by addition of EDCI (0.230 g, 1.48 mmol), DMAP (0.181 g, 1.48 mmol) and TEA (0.2 ml, 1.40 mmol) at once. The reaction mixture stirred overnight at room temperature. Reaction completion was checked by TLC analysis. The reaction mixture was then diluted in chloroform followed by washing with 1M HCl then NaHCO3 10%, and water to remove excess DMF. The crude produced after evaporation was washed with methanol and 2-4 drops of HCl and was filtered to remove excess amine, the white-coloured solid of TPE-1 was obtained (0.4 g, 43%). ¹H NMR (300 MHz, CDCl₃) δ 7.13-6.96 (m, 38H), 2.33-2.28 (m, 4H), 1.70-1.58 (m, 4H), 1.34-1.27 (m, 8H); ¹³C NMR (75 MHz, CDCl₃) δ 171.1, 143.7, 143.6, 132, 131.4, 131.3, 127.8, 127.7, 127.6, 126.4, 126.3, 118.7, 77.4, 77, 76.6, 37.7, 29, 28.9, 25.4; Mass (ESI): m/z = HRMS m/z: calculated for
C_{62}H_{56}N_{2}O_{2} 861.1420, found 861.1427 (M)^+ found; Elemental analysis for C_{62}H_{56}N_{2}O_{2}: calculated = C, 86.48; H, 6.56; N, 3.25; found = C, 86.53; H, 6.62; N, 2.87.

Synthesis of **TPE-2**: Decanoic acid (0.2 g, 1.2 mmol) and amino-TPE (0.243 g, 0.64 mmol) added to DMF (8 ml) at 0 °C and stirred for 10 min under nitrogen atmosphere, EDCI (0.218 g, 1.4 mmol) followed by DMAP (0.235 g, 1.92 mmol) and TEA (0.1 ml, 0.71 mmol) were added into the mixture. The reaction runs overnight in room temperature. Reaction completion was checked by TLC analysis. Crude was purified by column chromatography using Hexane and DCM to obtain **TPE-2** as a white colour solid (0.22 g, 64%). ^1H NMR (300 MHz, CDCl3) δ 7.14-6.97 (m, 19H), 2.34-2.29 (m, 2H), 1.75-1.59 (m, 2H), 1.33-1.29 (m, 12H), 0.92-0.88 (m, 3H); ^13C NMR (75 MHz, CDCl3) δ 171.1, 143.7, 143.6, 140.7, 140.3, 139.5, 136.2, 132, 131.4, 131.3, 127.8, 127.7, 127.6, 126.5, 126.4, 126.3, 118.7, 77.4, 77.2, 77, 76.6, 37.9, 31.8, 29.4, 29.3, 29.2, 25.6, 22.6, 14.4; HRMS m/z: calculated for C_{36}H_{39}NO 501.7140, found 501.7148 (M)^+; Elemental analysis for C_{36}H_{39}NO: calculated= 86.18; H, 7.84; N, 2.79, found = C, 86.21; H, 7.91; N, 2.82,
$^1$H NMR of TPE-1

$^{13}$C NMR of TPE-1
$^1$H NMR of TPE-2

$^{13}$C NMR of TPE-2
Chapter 3 Applied Sciences

Article

Influence of Odd and Even Alkyl Chains on Supramolecular Nanoarchitecture via Self-Assembly of Tetraphenylethylene-Based AlEgens

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Abstract: The Tetraphenylethylene (TPE) based dumbbell shaped molecules TPE-Pi, TPE-Su, TPE-Az, and TPE-Se were synthesised bearing odd-even alkyl chains containing 7, 8, 9 and 10 carbons respectively. These molecules reveal typical Aggregation Induced Emission (AIE) behaviour. The influence of the odd or even alkyl chain length was shown by studying the morphology of self-assembled nanostructures formed in a range of tetrahydrofuran (THF)/water solvent systems. For example, with a water fraction of 80%, TPE derivatives with odd alkyl chains (TPE-Pi and TPE-Az) self-assembled into nanosphere structures, while TPE-Su with 8 alkyl chains formed microbelts and TPE-Se with 10 alkyl chains aggregated into flower-like superstructures. These TPE derivatives also revealed interesting mechanochromic properties upon grinding, fuming and heating, which reveal the importance of molecular stacking in the crystal structure to the luminescent properties of the aggregates. The mechanochromic properties of TPE-Pi, TPE-Su, and TPE-Az were also demonstrated by the process of grounding, fuming, and heating.

Keywords: nanostructures; odd-even effect; self-assembly; tetraphenylethylene; mechanochromic properties

1. Introduction

Self-assembly of fluorescent π-conjugated small molecules into well-defined 1D, 2D and 3D nanostructures has proven to be an interesting strategy for fabricating functional devices with potential applications in chemosensors, biosensing, nanotechnology, biotechnology and optoelectronics [1–8]. A disadvantage of conventional organic fluorophores is that they show aggregation-induced quenching (AIE) effects due to the formation of excimers or exciplexes [9]. To overcome this drawback, in 2001 Tang et al. investigated, for the first time, the Aggregation-Induced Emission (AIE) phenomenon [10]. AIE fluorophores emits upon aggregation, whereas it is non-emissive when dissolved well in solution [11]. Thus, AIE fluorophores are an ideal building block for fabricating nanostructures with luminescent properties [12]. Tetraphenylethylene (TPE) and its derivatives have shown interesting AIE properties in the solid state due to its unique structure [13]. These AIE fluorophores have been employed to construct self-assembled fibers, nanowires, microrods, microtubes, hollow microspheres, microparticles, microlongs, microparticles, bird nest-like and flower-like structures, and helical morphologies in tetrahydrofuran (THF)/water solvent systems [14–25]. These molecular assemblies

derive from weak non-covalent interactions, such as hydrogen bonding, electrostatic interactions, π-π stacking, van der Waals forces and solvophobic interactions. The favourable properties of TPE make it a candidate for applications in chemosensors, biosensors and optoelectronic materials such as field-effect transistors (FETs), organic light emitting diodes (OLEDs) and solar cells [26–33]. The performance of an optoelectronic material is dependent upon the intermolecular interactions and emission efficiencies of the π-conjugated molecules that it is made from. Therefore, the design, synthesis and development of molecules with high solid-state efficiencies is central to the requirements of materials for optoelectronic applications.

We recently reported the self-assembly of a dumbbell-shaped TPE derivative connecting to an alkyl chain via an amide bond [34]. Scanning Electron Microscopy (FE-SEM) images revealed that this compound had self-organised into a flower-like assembly through a combination of amide-hydrogen bonding and van der Waals interactions. With these results in hand, in order to study the influence that alkyl chain length has on the self-assembly and optical properties of dumbbell shaped TPE molecules, we prepared compounds TPE-Se, TPE-Az, TPE-Su and TPE-Pi, possessing n-decyl, n-nonyl, n-octyl and n-heptyl alkyl chains, respectively (Scheme 1), and studied their morphology after self-assembly and AIE behaviour.

![Scheme 1. Synthesis of dumbbell shaped TPE-Se, TPE-Su, TPE-Az and TPE-Pi.](image)

2. Materials and Methods

2.1. Materials

Decanedioic acid (sebacic acid), octanedioic acid (suberic acid), nonanedioic acid (azelaic acid), heptanedioic acid (pimelic acid), tetraphenylethylene, triethyl amine, EDCl, DMAP and DMF were purchased from Sigma-Aldrich, St. Louis, MO, USA. All reactions were carried out under an argon atmosphere with dry solvents that had been degassed for 10–15 min with argon. Final compounds were purified using silica-gel column chromatography. $^1$H-NMR, $^{13}$C-NMR spectra were recorded on a Bruker Avance-300 MHz spectrometer, or a Bruker Advance 75 MHz spectrometer at 300 °K. Chemical shifts (in ppm) were referenced to TMS (Tetramethylsilane) as an internal standard. All measurements were performed in deuterated chloroform (CDCl$_3$). IR-Spectra were recorded by using a Thermo Nicolet Nexus 670 spectrometer (New Boston Street, Woburn, MA, USA) in the form of non-hygrosopic KBr pellets. UV-Vis spectra of pure precursor compounds were recorded using a Shimadzu UV-1800 spectrophotometer (Chiyoda-ku, Tokyo, Japan) at room temperature. Fluorescence emission spectra were collected using a Jobin-Yvon Horiba FluoroMax-4 instrument (Chiyoda-ku, Tokyo, Japan).
2.2. Spectroscopic Measurements

Sample preparation: Stock solutions of TPE-Se, TPE-Su, TPE-Az and TPE-Pi (1 × 10⁻⁴ M) were prepared in THF. A 0.2 mL aliquot of the stock solution of each was transferred separately to different volumetric flasks and made up to a 2 mL volume with respective solvents. The solutions were allowed to equilibrate for 2 h prior to casting onto a silicon substrate for Scanning Electron Microscopy (SEM) measurements.

UV-Visible Measurements: UV-Vis absorption spectra in mixed solvents were recorded in a Cary-50 in a 1 cm path length cuvette. The solutions were allowed to equilibrate at room temp for 2 h before spectral measurements.

Fluorescence Measurements: Fluorescence emission spectra were recorded on a Jobin-Yvon Horiba FluoroMax-4 instrument in a 1 cm path length cuvette. The solutions were allowed to equilibrate at room temp for 2 h before spectral measurements.

2.3. SEM Imaging

The silicon wafer substrate was cleaned with acetone, ethanol and then Milli Q water. SEM samples were prepared by solvent evaporation onto this silicon wafer and then sputter coated with gold for 10 s at 0.016 mA Ar plasma (SPI, West Chester, PA, USA), followed by FE-SEM imaging using a FEI Nova NanoSEM (Hillsboro, OR, USA) operating under high vacuum, which provided direct visualisation of the self-assembled aggregated structures.

2.4. Mechanochromism Study

The as-synthesized compounds were ground with a pestle and mortar for 5 min. The fumed samples were prepared by fuming the ground powders with acetone for 60 s. The fumed samples were heated at a temperature of 120 °C for 10 min.

Synthesis of TPE-Se: This was molecule prepared following our reported paper [34]. Sebacic acid (0.1 g, 0.5 mmol) and amino-TPE (0.147 g, 1.08 mmol) were added to DMF (6 mL) at 0 °C and stirred for 10 min under nitrogen atmosphere, followed by addition of EDCI (0.230 g, 1.48 mmol), DMAP (0.181 g, 1.48 mmol) and TEA (0.2 mL, 1.40 mmol) at once. The reaction mixture was stirred overnight at room temperature. Reaction completion was checked by TLC analysis. The reaction mixture was then diluted in chloroform followed by washing with 1 M HCl then NaHCO₃ 10%, and water to remove excess DMF. The crude produced after evaporation was washed with methanol and 2–4 drops of HCl and was filtered to remove excess amine, resulting in the white-coloured solid of TPE-4 (0.4 g, 43%). ¹H-NMR (300 MHz, CDCl₃) δ ppm: 7.13–6.96 (m, 39H), 2.33–2.28 (m, 4H), 1.70–1.58 (m, 4H), 1.34–1.27 (m, 8H). ¹³C-NMR (75 MHz, CDCl₃) δ ppm: 171.1, 143.7, 143.6, 132.0, 131.4, 131.3, 126.4, 126.3, 118.7, 37.7, 29.0, 28.9, 25.4; Mass (ESI) m/z: calculated for C₆₃H₇₃N₂O₂ 860.43, found: 860.41 (M⁺); Elemental analysis for C₆₃H₇₃N₂O₂: calculated = C, 86.48; H, 6.56; N, 3.25; found = C, 86.53; H, 6.62; N, 3.28.

Synthesis of TPE-Az: Azelaic acid (0.1 g, 0.5 mmol) and amino-TPE (0.406 g, 1.08 mmol) were added to DMF (8 mL) at 0 °C and stirred for 10 min under an argon atmosphere, followed by addition of EDCI (0.230 g, 1.48 mmol), DMAP (0.181 g, 1.48 mmol) and TEA (0.2 mL, 1.40 mmol) all at once. The reaction mixture was stirred overnight at room temperature. Reaction completion was checked by TLC analysis. The reaction mixture was then diluted in chloroform followed by washing with 1 M HCl, then NaHCO₃ 10%, and then water to remove excess DMF. The crude produced after evaporation was washed with methanol and 2–4 drops of HCl and, after filtration to remove excess amine, the white-coloured solid TPE-Az was obtained (73%). ¹H-NMR (300 MHz, CDCl₃) δ ppm: 7.13–6.96 (m, 39H), 2.33–2.28 (m, 4H), 1.70–1.58 (m, 4H), 1.34–1.27 (m, 8H). ¹³C-NMR (75 MHz, CDCl₃) δ ppm: 171.19, 142.76, 141.64, 137.38, 135.32, 128.43, 127.37, 121.75, 37.74, 29.01, 28.90, 25.40; Mass (ESI) m/z: calculated for C₆₃H₇₃N₂O₂ 846.41, found 846.40 (M⁺); Elemental analysis for C₆₃H₇₃N₂O₂: calculated = C, 86.49; H, 6.43; N, 3.31; found = C, 86.53; H, 6.62; N, 3.35.
Synthesis of TPE-Su: Suberic acid (0.1 g, 0.5 mmol) and amino-TPE (0.460 g, 1.22 mmol) were added to DMF (8 mL) at 0 °C and stirred for 10 min under an argon atmosphere, followed by addition of EDCl (0.230 g, 1.48 mmol), DMAP (0.181 g, 1.48 mmol) and TEA (0.2 mL, 1.40 mmol) all at once. The reaction mixture was stirred overnight at room temperature. Reaction completion was checked by TLC analysis. The reaction mixture was then diluted in chloroform followed by washing with 1 M HCl then NaHCO₃ 10%, and finally water to remove excess DMF. The crude product after evaporation was washed with methanol and 2–4 drops of HCl, and was filtered to remove excess amine, obtaining a white-coloured solid of TPE-Su (52%). ¹H-NMR (300 MHz, CDCl₃) δ ppm: 7.26–6.93 (m, 38H), 2.35–2.30 (m, 4H), 1.73–1.66 (m, 4H), 1.34–1.27 (m, 4H). ¹³C-NMR (75 MHz, CDCl₃) δ ppm: 174.5, 141.0, 140.0, 137.7, 135.1, 128.7, 128.3, 128.1, 127.9, 121.5, 38.3, 27.9, 25.5. Mass (ESI) m/z: calculated for C₉₀H₁₄₂N₂O₁₂ 832.40, found 832.52 (M⁺); Elemental analysis for C₉₀H₁₄₂N₂O₁₂: calculated = C, 86.50; H, 6.29; N, 3.36; found = C, 86.53; H, 6.32; N, 3.39.

Synthesis of TPE-Pi: Pimelic acid (0.1 g, 0.5 mmol) and amino-TPE (0.510 g, 1.36 mmol) were added to DMF (8 mL) at 0 °C and stirred for 10 min under a nitrogen atmosphere, followed by addition of EDCl (0.230 g, 1.48 mmol), DMAP (0.181 g, 1.48 mmol) and TEA (0.2 mL, 1.40 mmol) all at once. The reaction mixture was stirred overnight at room temperature. Reaction completion was checked by TLC analysis. The reaction mixture was then diluted in chloroform followed by washing with 1 M HCl then NaHCO₃ 10%, and then water to remove excess DMF. The crude product obtained after evaporation was washed with methanol and 2–4 drops of HCl and was filtered to remove excess amine, obtaining a white-coloured solid of TPE-Pi (51%). ¹H-NMR (300 MHz, CDCl₃) δ ppm: 7.11–6.95 (m, 38H), 2.37–2.33 (m, 4H), 1.80–1.73 (m, 4H), 1.34–1.27 (m, 2H). ¹³C-NMR (75 MHz, CDCl₃) δ ppm: 171.57, 140.72, 140.49, 138.18, 131.49, 131.17, 131.12, 128.34, 128.24, 118.77, 36.69, 28.72, 25.34. Mass (ESI) m/z: calculated for C₉₀H₁₄₂N₂O₁₂ 818.38, found 818.42 (M⁺) found; Elemental analysis for C₉₀H₁₄₂N₂O₁₂: calculated = C, 86.52; H, 6.15; N, 3.42; found = C, 86.56; H, 6.18; N, 3.46.

3. Results

The TPE derivatives TPE-Se, TPE-Az, TPE-Su and TPE-Pi were synthesised via amide coupling of amino-TPE and alkyl-dicarboxylic acids catalysed by 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDCI) and 4-dimethylaminopyrimidine (DMAP) in dry DMF (Scheme 2) under a nitrogen atmosphere. The synthesised compounds were fully characterised using ¹H-NMR, ¹³C-NMR, ESI-mass and FTIR spectroscopic techniques (Figures S1 and S4–S13).

Scheme 2. Structures of dumbbell shaped TPE-Se, TPE-Su, TPE-Az and TPE-Pi derivatives.

The Luminescent properties of TPE-Az, TPE-Su and TPE-Pi under ambient conditions were examined in the THF/water solvent system as shown in Figure 1. In THF, all three TPE derivatives (i.e., TPE-Az, TPE-Su and TPE-Pi) exhibited faint blue emission in solution. Upon incremental addition of water, green fluorescence was first observed at 80% water. Furthermore, in THF/water
solution containing 90% water, we observed strong fluorescence with a higher intensity, indicating an aggregated state of the molecules displaying AIE. The emission colour and intensity change of solution could be readily visualised with the naked eye (Figure 1A–C). The remarkable emission enhancement for TPE-Az, TPE-Su and TPE-Pi is highly reproducible. Here we presume that amide hydrogen bonding and van der Waals interactions are involved in the aggregation process of the TPE derivatives.

![Photographic images of TPE-Az, TPE-Su and TPE-Pi](image)

Figure 1. Luminescence properties: photographic images of (A) TPE-Az (B) TPE-Su (C) TPE-Pi in THF-water solvent mixtures with $f_w$ values of 0%, 20%, 40%, 60%, 80% and 90% respectively, irradiated at 365 nm.

### UV-Vis Absorption and Fluorescence Properties

UV-Vis absorption spectroscopy was employed to investigate the photophysical properties of TPE-Se, TPE-Az, TPE-Su and TPE-Pi (Figure 2). The electronic spectra of $1 \times 10^{-5}$ M solutions of TPE-Se, TPE-Az and TPE-Pi showed absorption bands at 325 nm and 260 nm in THF, corresponding to $\pi-\pi^*$ transitions. The UV-Vis spectrum of compound TPE-Su in the same solvent displayed the same absorption maxima at 325 nm but the shoulder peak at 260 nm was absent. It should also be noted that the shoulder peak for TPE-Se was bathochromically shifted by around 10 nm to 270 nm relative to the other compounds. After establishing the absorption properties of TPE-Se, TPE-Az, TPE-Su and TPE-Pi, the emission properties of the four compounds were measured in THF solution. None of these four compounds showed photoluminescence in THF solution (Figure 3A–C and Figure S2). However, upon incremental addition of water to THF solutions of TPE-Se, TPE-Az, TPE-Su and TPE-Pi, the emission intensity for all four compounds was enhanced. In Figure 3A, the fluorescent emission properties of TPE-Az are shown. Compound TPE-Az was non-fluorescent in THF solution. With the addition of water to the THF solution of TPE-Az, fluorescence emission intensity remained unchanged for $f_w = 10-60\%$ H$_2$O/THF solutions. A slight change in intensity was observed at $f_w = 70\%$. At $f_w = 80\%$, a significant 90-fold fluorescence emission intensity enhancement was observed. The
emission peak was split into two peaks at 435 nm and 535 nm at $f_w = 90\%$, with an emission enhanced by 120 times compared to pure THF solution. The photoluminescent spectra of TPE-Su are shown in Figure 3B. Once again, a THF solution of TPE-Su did not show any emission. Upon incremental addition of water (10–60%) to THF solution, no emission spectral changes were observed. When the water fraction was increased to 70–80%, the emission spectra showed two split peaks at 395 nm and 535 nm, with a 120-fold increase in emission intensity compared to pure THF. Furthermore, in the THF/water (90%) mixture the peak at 395 showed a 30 nm red-shift, and the peak at 535 nm showed a 40 nm blue-shift. The new emission bands for TPE-Su at $f_w = 90\%$ appeared at 425 nm and 495 nm. Similar studies were carried out for compound TPE-Pi in THF with increasing amounts of water (Figure 3C). Emission spectral changes were not observed for an increase in the water fraction between $f_w = 10–40\%$. A further increase in water fraction to $f_w = 50\%$ resulted in a slight increase in emission intensity. With a water fraction of 70%, a 110-fold emission peak enhancement was observed at 475 nm compared to emission in pure THF. At $f_w = 80\%$, the emission peak was blue-shifted to 460 nm, and a further increase of water fraction to 90% led to a split emission peak, at 450 nm and 525 nm. Figure S2 displays the steady-state fluorescence spectra of the compound TPE-Se in THF and in THF/water solvent mixture. At first, the addition of water (10–50%) to THF solution resulted in no change in the emission spectra of TPE-Se. But when the water fraction was increased to 60% to 80%, an increase in emission intensity was observed. At $f_w = 90\%$ the emission peak split into two peaks at 435 nm and 535 nm with rapid enhancement of intensity. Both peaks were red-shifted by 25 nm compared to $f_w = 80\%$. This is a clear demonstration of the AIE behaviour of TPE-Se aggregates via self-assembly. We can conclude that, to achieve maximum emission intensity, a high fraction of water ($f_w = 80–90\%$) is required. The addition of a water fraction (9–90%) to THF solution strongly influences the emission properties of these compounds with respect to peak position and peak intensities (Figure 3D). From fluorescence emission, it can be clearly seen that steady increment of the fluorescent intensity was observed up to 90% water content, with red-shifted peak intensity. However, with a further increase of the water fraction >98%, a decrease in intensity was observed, which is due to the larger aggregates and precipitation of self-assembled structures from the solution, as resulting in only a small amount of AIGs being involved in emission. The comparative investigation of emission properties in THF/water clearly suggested that the compound structures TPE-Se, TPE-Az, TPE-Su and TPE-Pi are dramatically affected in $f_w = 90\%$. These results clearly demonstrate that the phenyl ring of TPE around the alkyl chains is restricted in the aggregated state due to the restricted intramolecular rotation (RIR), the mechanism model for the aggregation-induced emission (AIE) phenomenon. The bulky TPE moieties impair the intermolecular π-π stacking. Thus, the increased FL intensity upon aggregation in higher water content compared to in the dilute THF solutions is because the mechanism for consuming the excitation energy is switched out, similar to earlier report by Tang group [10].

![Figure 2. The UV-Vis absorption spectra of TPE-Se, TPE-Az, TPE-Su and TPE-Pi (10 μM).](image-url)
Figure 3. The fluorescence emission spectra of (A) TPE-Az, (B) TPE-Su, (C) TPE-Pi (10 μM) in THF/water at various water fractions (λex = 365 nm) and (D) The fluorescence intensity changes of TPE-Se, TPE-Az, TPE-Su and TPE-Pi at 475 nm as a function of water fraction in THF solvent mixture.

In order to elucidate the aggregation behaviour of TPE-Se, TPE-Az, TPE-Su and TPE-Pi in THF/water, as well as the effect of the number of carbons in the alkyl chains on assembly, SEM studies in the presence of various fractions of water/THF were undertaken to observe the morphology of aggregates produced from TPE-Se, TPE-Az, TPE-Su and TPE-Pi, and images are shown in Figure 4 and Figure S2. Figure 4A shows the morphology produced from TPE-Pi aggregation in a THF/water mixture with the water fraction at 80%. It can be clearly seen that, under these conditions, the TPE-Pi (with an odd number of carbons in the alkyl chain of 7) assembled into well-defined nanospheres, with diameters in the range of 200–1000 nm. A further increase in the water fraction (f_w = 90%) led to the collapse of the nanospheres into nanobeads, as shown in ESI Figure S3A. When the odd alkyl chains in the TPE compound was increased to 9 (TPE-Az), the morphology of the aggregates in the THF/H_2O are remained as spheres, ranging in diameter from 50–500 nm with f_w = 80% (Figure 4B) and nanobeads with f_w = 90% (ESI Figure S3B). Interestingly, when the number of carbons in the alkyl chains of the compound are even (TPE-Su with 8 alkyl carbons and TPE-Se with 10 carbons), different morphologies were observed. With the alkyl chain of 8 carbons, microbelts with a width of 5 μm and a length of a hundred μm were obtained when the TPE-Su was assembled at f_w = 80% (Figure 4C). However, similar to TPE-Az and TPE-Pi, only TPE-Su nanobeads were observed upon further addition of water (f_w = 90%) (ESI Figure S3C). With an alkyl chain of 10 carbons, we recently reported the morphologies of dumbbell shaped TPE-Se in THF/water at different water fractions [34]. Herein, at f_w = 80%, self-assembly of TPE-Se led to flower-like aggregates several micrometers in diameter (Figure 4D). These microflowers were composed of several fractal nanostructures grown from the centre of the flower. These microflowers also disappeared with a water fraction of higher than
90% (ESI Figure S3D). TPE-based dumbbell-shaped molecules TPE-PI, TPE-Su, TPE-Az, and TPE-Se bear odd and even numbers of carbons in the alkyl chains, of 7, 8, 9 and 10, respectively. In particular, odd numbers of carbons (7 and 9) in the alkyl chains gives mismatching packing, producing particular aggregates. Importantly, even numbers of carbons (8 and 10) in the alkyl chains produces a flat, belt-like morphology, and in case of 10 carbons in the alkyl chains produces a flower-like morphology due to the fractal of TPE-Se growing from centre of the flowers. These results are similar to the odd-even effect in supramolecular self-assembly [25], in which odd numbers of carbons in the alkyl chains produces a loosely packed pattern in anti-parallel alignment, and exhibits particular aggregates because of the increased intermolecular interactions. However, even numbers of carbons in the alkyl (perfectly matching) chains pack tightly, and produce fibris networks with parallel packing.

![Image](image_url)

**Figure 4.** FE-SEM images of aggregates formed from (A) TPE-PI, (B) TPE-Az, (C) TPE-Su and (D) TPE-Se in THF/water with water fraction of 80%.

The mechanochromic properties of TPE-PI, TPE-Su, and TPE-Az were also investigated by the process of grinding, fuming, and heating, as shown in Figure 5A-C. The molecular packing of these compounds led to strong emissions in the solid state. This is direct evidence of the AIE effect in these compounds, where the stacking of the TPE moieties as a result of aggregation restricts non-radiative relaxation pathways, and this stacking persists in the solid state. The emission colour and intensity of the powder form are similar to those observed after self-assembly of these compounds in water/THF mixture, suggesting that the structure of the aggregates suspended in solution and the solids were similar. However, the emission intensity of the resulting materials was significantly decreased after grinding. This may be due to the reduction in the crystallite size. Even after fuming with acetone, the ground materials did not revert to their initial luminescent states in terms of either colour or intensity. However, when heating was applied, while the luminescent state was insignificantly altered, the luminescent colours of both TPE-PI and TPE-Az changed from bright blue to light green. The TPE-Se also showed significant mechanochromic properties, as reported in our previous work [34]. These results confirm that these AIGs are relatively sensitive to molecular stacking in the crystal structure.
Figure 5. The mechanochromic properties of (A) TPE-PI, (B) TPE-Su, and (D) TPE-Az, showing the luminescence changing of these compounds after grinding, fuming and heating.

4. Conclusions

Tetraphenylethylene (TPE)-based dumbbell-shaped molecules TPE-PI, TPE-Su, TPE-Az, and TPE-Se bearing an odd-even number of carbons in alkyll chains of 7, 8, 9 and 10, respectively, were synthesised. The solvophobic-controlled self-assembly, as well as luminescent properties of these compounds, were studied in detail. Similar to other TPE derivatives, TPE-PI, TPE-Su, TPE-Az, and TPE-Se showed typical AIE behaviour, being non-emissive in THF solution and emitting strongly in THF/water mixture due to self-assembly of aggregates. With a water fraction of 80%, while TPE derivatives with odd alkyll chains (TPE-PI and TPE-Az) self-assembled into nanosphere structures, TPE-Su with 8 carbons in the alkyll chain formed microbelts and TPE-Se with 10 carbons in the alkyll chain aggregated into flower-like superstructures. These TPE derivatives also revealed interesting mechanochromic properties upon grinding, fuming and heating, revealing the sensitivity of luminescent properties to molecular stacking in the crystal structure and crystallite size. The results described in this paper can be employed to pursue further strategies in component design and self-assembly theory that go beyond simple morphologies.

Supplementary Materials: The following are available online at http://www.mdpi.com/2076-3417/7/11/1119/s1. The following ESi are available online for compounds (A) TPE-PI, (B) TPE-Az, (C) TPE-Su and (D) TPE-Se. Figure S1: FTIR, Figure S2: Fluorescence emission spectra of TPE-Se. Figure S3: FE-SEM images of the suspension of (A) TPE-PI, (B) TPE-Az, (C) TPE-Su and (D) TPE-Se in THF/water with a water fraction of 90%.

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Author Contributions: M.S. performed synthesis and structure determination using spectroscopic techniques along with UV/vis and fluorescence spectroscopy. D.D.L. performed surface-based assembly to visualise the nanostructures by SEM. S.V.B. (ICT) drafted the first draft of the manuscript, and I.A.J. corrected the manuscript and co-supervised the D.D.L. S.V.B. (RMIT) directed the research, interpreted and analysed the data, and wrote the full manuscript. All co-authors reviewed the manuscript.

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Supplementary Materials: Influence of Odd and Even Alkyl Chains on Supramolecular Nanoarchitecture via Self-Assembly of Tetrphenylethylene-Based AIEgens

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1. Supplementary Information

Figure S1 FTIR spectra of TPE-Pl, TPE-Ar, TPE-Su and TPE-Se.

Figure S2. The fluorescence emission spectra of TPE-Se.
**Figure S3.** FE-SEM micrograph images of the suspension of (A) TPE-Fl, (B) TPE-Az, (C) TPE-Su and (D) TPE-Se in THF/water with water fraction of 90%.

2. Spectra’s of TPE derivatives

**Figure S4.** 1H NMR spectrum of TPE-Se.
Figure S5. $^{13}$C NMR spectrum of TPE-Se.

Figure S6. ESI Mass spectrum of TPE-Se.
Figure S5. $^1$H NMR spectrum of TPE-Az.

Figure S6. $^{13}$C NMR spectrum of TPE-Az.
Figure S9. ESI Mass spectrum of TPE-Az.

Figure S10. $^1$H NMR spectrum of TPE-Su.
Figure S11. $^{13}$C NMR spectrum of TPE-Su.

Figure S12. ESI mass spectrum of TPE-Su.
Figure S13. $^1$H NMR spectrum of TPE-Pl.

Figure S14. $^{13}$C NMR spectrum of TPE-Pl.
Figure S15. ESI mass spectrum of TPE-Pi.
Chapter 4 Conclusions & Future Directions
4.1 Summary and Perspective

It used to be a general concept that a poor emitter in the solution state will not emit systematically in the solid state. However, AIEgens have gained a considerable reputation as functional materials that shine more in the solid state than in solution. In aggregate form these materials overcome classic problems caused by the ACQ effect, which limits the use of luminescent materials in the solid state. The dynamic intramolecular motions, also known as the low-frequency modes of the reorganization energy, diminish excitons of the AIE luminogens, while the restriction of intramolecular rotation (RIR) process activated by the aggregate formation greatly boosts their light emissions.

In this thesis, 5 newly synthesized derivatives of TPE-based AIEgens have been studied. Their structure-property relationships have been scrutinized, their mechanistic behaviour examined, & their potential applications predicted. A wider insight into AIE mechanisms and advocated RIM (restriction of intramolecular motions) processes, described as the main cause for the AIE phenomena has been established. Upon the formation of nano-clusters, the electron-rich groups blend into one another to share their unpaired electrons and work as “congregated chromophores” with shrunk energy gaps. In other words, the dynamic intramolecular motions, in other words, the low-frequency modes of the reorganization energy, obliterate the excitons of the AIE luminogens, while the restriction of intramolecular rotation process triggered by the aggregation.

The most important applications of AIEgens are situated in the domains of life science and biomedical engineering. AIEgen nanoparticles can be used for in-vitro and in-vivo imaging of biogenic molecules, cells, tissues, organisms, etc. The bright emission, elevated efficiency, exceptional photostability, prominent biocompatibility, and their optical nonlinearity present them as promising candidates for imaging and tracing applications.
This thesis mainly discussed the synthesis of Tetraphenylethylene (TPE)-based derivatives, and their use for supramolecular self-assembly.

4.1.1 Chapter 2- Flower-like self-assembly of two TPE derivatives
In this chapter, the formation of micrometer-sized flower-like supramolecular structures was achieved by hierarchical self-assembly of tetraphenylethene (TPE) derivatives in aqueous–organic solvent mixture media for the first time. It is noteworthy that the flower-like microstructures several micrometers in size (10–30 μm) are composed of flake-like nanostructures several nanometers in thickness. The formation of such flower-like fractal assemblies is attributed to a balance between the intermolecular interactions, including the π–π interaction that requires a perfect stacking alignment and H-bonding, and van der Waals interactions that demand a torsion adjustment angle to circumvent the barrier in the self-assembly, which leads to a smaller intermolecular torsion angle. This permits the molecule to form supramolecular assemblies in a controlled 3D fashion. Similar to many other TPE derivatives, TPE-1 and TPE-2 show AIE behavior in the aggregated state that can form in a solvent media such as high water fraction mixtures with organic solvents. Interestingly, TPE-2 in THF/water ($f_w = 85\%$) self-assembled into flower-like structures. However, TPE-1 assembled into spheres in similar water contents and dual centred two-lobe-surface initiated fractal growth in CHCl$_3$/hexane upon solvent evaporation.

4.1.2 Chapter 3- Odd & Even effect in TPE derivatives
Other TPE derivatives with 9, 8 and 7 carbons led to self-assembled structures dependent upon their odd-even structures. Even numbered peptide molecules the oxygen atoms can form a hydrogen bond with the lateral peptide on two sites, namely close to the head & terminal moieties, whereas the odd-numbered amides end up with the possibility of only one hydrogen bond which imposes an unstable packing. The final morphology of the odd- and even-numbered
derivatives clearly reflects the effect of packing, where the odd-numbered molecules led spherical self-assemblies, and even-numbered molecules that benefit from a stable packing owing to two hydrogen bonds, show flake-like flat morphology that eventually forms the flower-like 3D structure.

The SEM analysis specifically demonstrated the ability to build microstructures based on self-organization utilizing the solvophobic effect and molecular non-covalent interactions into well-formed and separate complex morphologies such as flowers. This may trigger further developments in molecular superstructural design based on self-assembly theory that goes beyond simple morphologies. To the extent of our knowledge, the flower-shaped morphology formed from an AIE-active molecule in the aqueous medium described here is the first example of such an assembly being observed in a supramolecular system containing a single molecule. The results delineated in this research project demonstrate a pragmatic pathway about how to deal with intermolecular interactions in molecular design, and proved that by utilizing solvophobic effects and thermal and mechanical stimuli supramolecular geometrical design and functionality can be controlled. Moreover, flower-like structures of AIE-active molecule built using solvophobic control illustrates their potential application in various domains in conjunction with other chemical structures.

4.1.3 Proposed mechanism for self-assembly of TPE derivatives in the aggregate form

By studying the electron microscopy images of the self-assembled alkyl-TPE, we believe that initially alkyl-TPE self-assembles into a supramolecular curved structure with the hydrophobic chains exposed externally to the polar solvent with the twisted structure being stabilised by intermolecular H-bonding in combination with π - π interaction of AIE-active TPE core.

The alkyl-TPE as an amphiphilic molecule in THF/Water solvent mixtures can take conformations where the polar groups of N-H and C = O of the
amid group are involved in internal and external H-bonding. The amide N–H is mainly involved in both the intermolecular and intramolecular H-bonding with carbonyl of the amide groups. Polar solvents further induce polarity in the alkyl-TPE molecular structure and empower the hydrophobic interactions between molecules producing curved or linear self-assembly. The curved supramolecular structures bury the alkyl chain on the internal side of the wall at the same time exposing the amide groups to produce hydrogen bonding with polar solvent on the exterior of the structure. Nonpolar solvents such as hexane and less polar solvents such as THF will strongly solubilise the alkyl chains preventing self-assembly and inclining towards a more symmetrical conformation.

Even numbers of carbons in the alkyl, as seen in the figure below, flawlessly matching chains pack tightly, and produce fibrils networks with parallel packing.

![An even-numbered example of packing.](image)

The odd numbers of carbons in the alkyl chains, on the contrary, produce a loosely packed pattern in anti-parallel alignment, and exhibits particular aggregates because of the increased intermolecular interactions.
An odd-numbered example of packing.

In amides, linear hydrogen bonds are feasible only in the case of the even homologues, because two alike distant CO-NH pairs occur on each edge of the chain. In the odd-numbered amides, however, both N-H groups and both C=O groups are placed on a single edge and the distances are not the identical. Linear hydrogen bonds are impossible to come to existence. The odd homologues turn out to be unstable because only one chain of linear hydrogen bonds is achievable.

### 4.2 Future Research

In a nutshell, this thesis work describes the synthesis of novel TPE derivatives with AIE activity and a further investigation of these derivatives formed via supramolecular self-assembly and also their mechanochromic features.

**Future perspectives:** The TPE derivatives are facile to synthesize and show favorable AIE activity in the solid state. The AIE activity of TPE luminogens is highlighted due to the emission enhancement in the solid and aggregate state as compared to the dissolved state. Although the advantageous points of AIE in TPE derivatives has led to them being used in many applications, there is still a requirement to consider using TPE derivatives for even further applications, namely solar cells & the sensing of bioactive molecules. Urea & TPE-based ion sensors may be considered in future plans. Background knowledge shows that urea has proved to be a crucial metabolite, produced as a protein degradation
product or utilized for the destruction of unused amino acids. Many urea sensors were appointed over the years, some depend on conductivity alternations due to the enzymatic reaction \(^2\&^3\) & some others lean on potentiometry \(^4\&^5\), amperometry \(^6\) and on an optical signal \(^7\&^8\).

Urease (E.C. 3.5.1.5), an enzyme that catalyzes the hydrolysis of urea to ammonium and bi-carbonate ions in the presence of water, works as shown below:

\[(\text{NH}_2)_2\text{CO} + 3\text{H}_2\text{O} \rightarrow \text{Urease} \ 2\text{NH}_4^+ + \text{OH}^- + \text{HCO}_3^-\]

Various urea biosensing schemes and devices developed to evaluate urease activity have emerged, counting on several kinds of transducers, such as pH electrode \(^9\) and a miniaturized Ion Selective Field Effect Transistor electrode (ISFET) \(^10\). Another example of this type has been a urea biosensor where urease was covalently linked to an electroactive polymer that demonstrated considerable stability and a detection range of 0.018–1.8 mg/dL \(^11\).

The future work consists of the design of a biosensor based on ion tracks, where the transduced signal relies on the ion generation and their flow in response to urea hydrolysis by urease.
4.3 Reference
