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AIEE Phenomenon: Tetraaryl *vs* Triaryl Pyrazoles

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Tetraarylpyrazoles are synthesized from commercially available materials in three steps and found to exhibit Aggregation Induced Emission Enhancement (AIEE) characteristics. By removing one aryl unit in the tetraarylpyrazole leads to Aggregation Caused Quenching (ACQ), thus, the number of aryl groups plays an important role to explore such phenomena.

Pyrazole is an interesting class of five-membered heterocyclic compound.[1] This motif shows remarkable activities in biological systems[2] (anti-inflammatory, anti-pyretic, anti-microbial, anti-viral, anti-depressant, agrochemicals etc.), optical sensors[3] (cosmetic colourings, optical brighteners, UV stabilizers, photoinduced electron transfer systems), suitable to stabilize various metal ions and effectively utilized as ligands in cross-coupling reactions.[4] Thus, the research is mainly focused on the synthesis of substituted pyrazole derivatives.[5] Although several excellent methods are known for the synthesis of substituted pyrazole derivatives in the literature,[6] developing a new protocol with an interesting property is always needed.[7]

The development of efficient luminophoric materials is of great interest for both fundamental research and practical applications. The main problem associated with the emission of most luminogenic materials in the solid state is Aggregation Caused Quenching (ACQ) effect which results in unsatisfactory efficiency during film formation, thereby preventing them from real world applications.[8] In order to solve this issue, Tang et al and Park et al discovered two novel photoluminescence phenomena such as Aggregation Induced Emission (AIE) and Aggregation Induced Emission Enhancement (AIEE) respectively.[9] Since then, researchers have developed wide range of AIE and AIEE active organic luminophoric materials revealing their applications in thin film display, light emitting technology etc.[10] Among them, 1,1,2,3,4,5-hexaphenylsilole (**1**) was the first AIE active molecule, which was non-emissive in

dilute solution, however, highly emissive upon aggregation due to its propeller orientation.[9a] Our ongoing interest in synthesis of 1,3,4,5-tetraphenyl-1H-pyrazole (**2a**, Ar¹ = Ar² = Ph),[11] which is closest analogue of **1**, will show AIE or AIEE characteristics? Herein we wish to report the synthesis of tetraarylpyrazole derivatives by simple and efficient synthetic methodology. Further, the AIEE behavior of pyrazole derivatives and the role of aryl groups on the photoluminescence properties are examined.
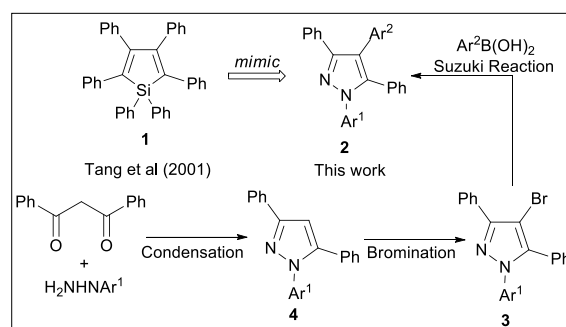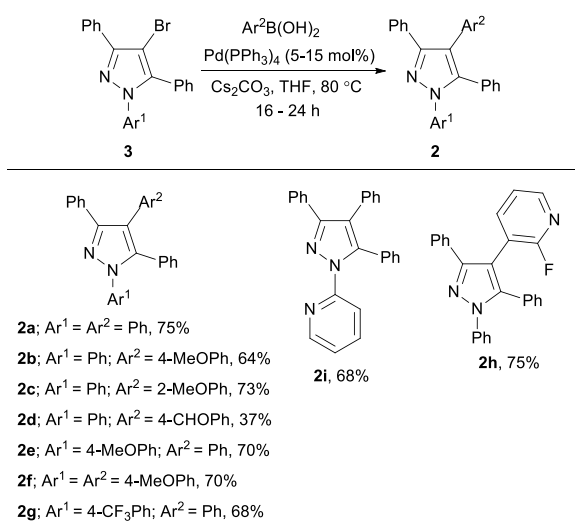

Chart 1

Synthesis of tetraarylpyrazoles are scarcely reported.[12,13] These methods suffer low yield, less substrate scope and multi-step syntheses of starting materials. Therefore, we envisioned a simple synthetic route to prepare the tetraarylpyrazoles **2** from commercially available materials in three steps (Chart 1). The key step of the synthetic route is Suzuki cross-coupling of 4-bromotriarylpyrazoles **3** with arylboronic acids. Thus, the required 4-bromotriarylpyraozles **3** were synthesized from 1,3-dicarbonyl compounds in two-steps. The first step is cyclocondensation of 1,3-diarylpropan-1,3-diketone with aryl hydrazines in refluxing acetic acid and then followed by N-bromosuccinimide bromination of the resulting pyrazoles **4** in CCl₄ (Schemes 1 & 2, ESI†).[14] Next, we focused on the key reaction of tetraarylpyrazoles synthesis. Thus, the reaction of 4-bromo-1,3,5-triphenyl-1H-pyrazole (**3a**, Ar¹ = Ph) with phenylboronic acid was carried out under typical Suzuki

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reaction conditions. However the expected 1,3,4,5-tetraphenyl-1H-pyrazole (**2a**) was not formed, instead, 1,3,5-triphenyl-1H-pyrazole (**4a**, Ar^1 = Ph) was obtained as major product via debromination. To overcome debromination product, we screened various reaction conditions to optimize Suzuki reaction of 4-bromopyrazole derivative **3a** with phenylboronic acid (Scheme 3, Table 1, ESI†). We found that 1.1 equiv of phenylboronic acid with 5 mol% of Pd(PPh$_3$)$_4$ in 1.5 equiv of Cs$_2$CO$_3$ in refluxing THF afforded the expected 1,3,4,5-tetraphenyl-1H-pyrazole (**2a**) in 75% yield (Scheme 1).

2a; Ar^1 = Ar^2 = Ph, 75%
2b; Ar^1 = Ph; Ar^2 = 4-MeOPh, 64%
2c; Ar^1 = Ph; Ar^2 = 2-MeOPh, 73%
2d; Ar^1 = Ph; Ar^2 = 4-CHOPh, 37%
2e; Ar^1 = 4-MeOPh; Ar^2 = Ph, 70%
2f; Ar^1 = Ar^2 = 4-MeOPh, 70%
2g; Ar^1 = 4-CF$_3$Ph; Ar^2 = Ph, 68%

2i, 68%

2h, 75%

Scheme 1 Synthesis of tetraarylpyrazoles **2a**-**2i**.

We examined various substituted arylboronic acids under similar reaction conditions. For electron donating group, 4-methoxyphenyl and 2-methoxyphenylboronic acids were effectively coupled with 4-bromopyrazole **3a** affording respective 1,3,4-triphenyl-4-(4-methoxyphenyl)-1H-pyrazole (**2b**) and 1,3,4-triphenyl-4-(2-methoxyphenyl)-1H-pyrazole (**2c**) in good yields (Scheme 1). Whereas electron withdrawing group such as -CHO substituted phenylboronic acid gave very low yields of **2d** (37%). Further, we studied electron donating and withdrawing groups effect on 1-N-aryl substituted pyrazole ring. These groups did not influence the yield of the cross-coupled products **2e-2g** (Scheme 1). However, 1-*N*-heteroarylpyrazole required higher catalyst loading (15 mol%) to obtain good yield of coupled product **2i**. Successfully, the heteroarylboronic acid was also coupled with **3a** affording 4-heteroaryl substituted pyrazole derivative **2h** in 75% yield.

The newly synthesized tetraarylpyrazoles are highly soluble in organic solvents, however, insoluble in water. The absorption spectrum of **2a** in acetonitrile showed a broad band between 250 and 400 nm attributed to the π to π* transition. In the fluorescence spectrum, the dilute solution of **2a** exhibits a weak emission band at 370 nm (Fig. S1b, ESI†), when excited at 280 nm with the quantum yield (Φ$_F$) of 0.17. These results are comparable to those of similar pyrazole derivatives.[7] Intriguingly, a dramatic change in fluorescence emission intensity is observed in the water-acetonitrile mixture. Up to 70% of water in acetonitrile/water mixture, the emission band at 370 nm is remained unchanged; however, as the water content

increased from 70% to 90%, the emission intensity at 370 nm is enhanced with the quantum yield (Φ$_F$) of 0.36, which is twofold higher as compared to **2a** in pure acetonitrile solution (Fig. 1a). Apparently, the emission of **2a** is boosted by aggregation thereby making it AIEE active. The intensity variation suggests that **2a** starts to aggregate as the water fraction reaches 70% and then, the aggregate continues to increase as the water content increases from 70% to 90% (Fig. 1a inset). Overall, when the water content increased to 70%, which reaches the critical limit, upon further addition of a small amount of water significantly promotes efficient pyrazole aggregation, leading to enhancement in the emission intensity.
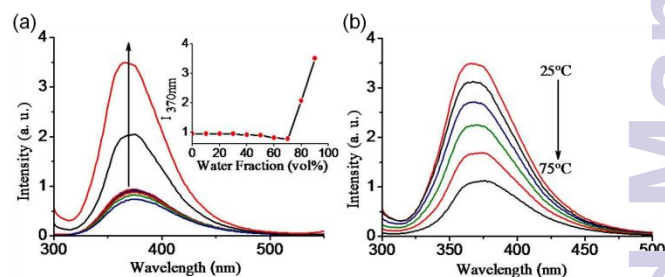

Fig. 1(a) Emission spectra of **2a** in acetonitrile/water mixtures with increasing amount of water (f_w=0-90 vol%). Inset shows the changes in the emission intensities of **2a** with the water contents in the acetonitrile/water mixture. (b) Temperature effect on the emission intensity of **2a** in acetonitrile/water (1:9 v/v), (λ$_{ex}$=280 nm)

Further, the effect of temperature on the emission spectrum of **2a** in the solvent mixture (1:9 v/v, acetonitrile/water) was also investigated (Fig. 1b). When the temperature was increased from 25 °C to 75 °C, the emission intensity at 370 nm was decreased gradually. These results suggest that the aggregated state of the compound at lower temperature breaks into monomer like state at higher temperatures. Thus, substantiates the mechanism of restricted intramolecular rotation (IMR) of the aryl groups upon aggregate formation. Overall, the aggregates at the low temperature are more rigid and more emissive than at higher temperature. Similar trend was observed in **2e** and **2i** (Fig. S5-8 for **2e** & S9-12 for **2i**, ESI†). The aggregate formation of **2a**, **2e** and **2i** at 90% of acetonitrile/water solvent mixture were further confirmed by dynamic light scattering (DLS) studies, where the particle sizes were found to be 150 nm, 224 nm and 172 nm, respectively. The nanoparticle size reflects an effective restriction in the IMR of the fluorophore, resulting in enhanced emission. The single crystal X-ray analysis of **2a** and **2i** further affirmed the restriction in IMR during aggregation.

The single crystal X-ray structure analysis is shown in Fig. 2a and 2b. As observed from the spectral analysis, four phenyl (**B**, **C**, **D** and **E** positions) units are connected with the pyrazole core. The phenyl units are deviated from the mean pyrazole plane with the tilt angle of 49.6° to 52.4° in **2a** and 50.8° to 53.1° in **2i** respectively. In order to avoid the steric crowding, the phenyl units are arranged in propeller fashion in the pyrazole core. The π-π interaction plays a major role for Aggregation Caused Quenching (ACQ).[9a] However, such interactions in the crystal analyses of **2a** and **2i** are not found, instead, we observe two

intermolecular hydrogen bonding interactions such as C-H…N and C-H…Ph(π) interactions. The crystal analysis of **2a** and **2i** generate two 1-D arrays through the intermolecular hydrogen bonding interaction (Fig. S14, 15 & S20, 21, ESI†), where three molecules of pyrazole are involved to generate such arrays and are formed between; (i) pyrazole N (N2), p-CH in the **B**-phenyl unit (C7-H7) of one molecule interacts with p-CH in the **E**-phenyl unit (C25-H25) of the second molecule and pyrazole N (N2) of third molecule with the distances and angles of C7-H7…N2 and C25-H25…N2 are 2.78 Å, 141° and 2.80 Å, 140° for **2a** and the respective values in **2i** are 2.66 Å, 133° and 2.70 Å, 145° (Fig. S14 & S18) respectively, and (ii) one of the CHs (C6-H6) in the **D**-phenyl ring and phenyl π cloud of **B**-ring (Ph-π) of one of the pyrazole unit interacts with phenyl π-cloud of **C**-ring of the second molecule and one of the CHs (C26-H26) in the **E**-phenyl ring of the third molecule with the distances and angles of C6-H6…Ph(π) and C26-H26…Ph(π) are 3.00 Å, 144° for **2a** and the respective values in **2i** are 3.05 Å, 144° and 2.92 Å, 145° (Fig. S15 & S21) respectively. Combining these two 1-D arrays, **2a** (Fig. 2c) and **2i** (Fig. S22, ESI†) generate 2-D supramolecular assembly in the solid state. Overall, the phenyl rings present in the pyrazole units are effectively packed in a propeller manner by the intermolecular hydrogen bonding interactions which restrict the intramolecular rotation of such units in the solid state, thus leads to emission enhancement, as observed in the aggregated state.
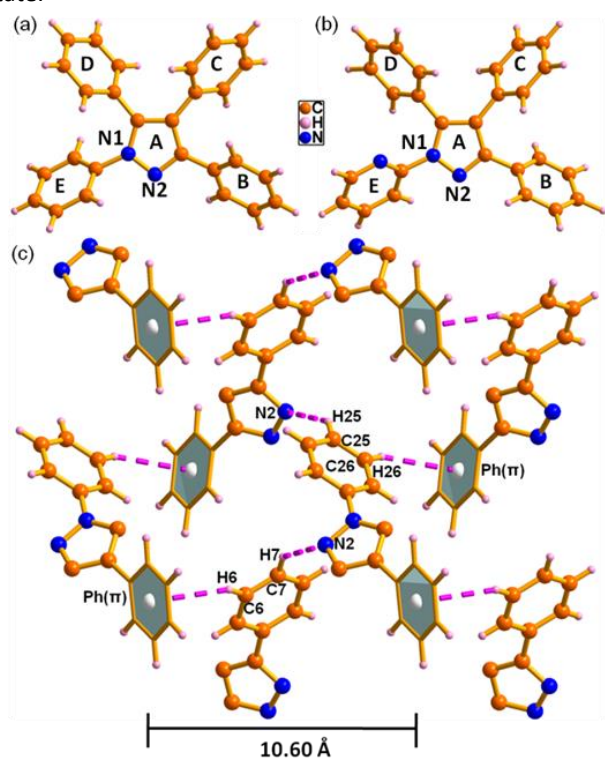

Fig. 2 Single crystal X-ray structure of **2a** and **2i**. (a & b) Top views of **2a** and **2i**. (c) 2-D array in **2a**. The aryl units which are not involved in the intermolecular hydrogen bonding interactions are omitted for clarity.

Now, the question is, whether all the four phenyl rings are really essential for generating AIEE phenomenon or not. In order to justify this, we further extended similar such experiments with 1,3,5-triphenyl-1*H*-pyrazole (**4a**). The 15μM

acetonitrile solution of **4a** showed an absorption band at 274 nm, when excited at this wavelength, which displayed an emission band at 360 nm. The similar experiments were performed by increasing the water fraction from 10% to 90% in the acetonitrile solution of **4a** (Fig. 3a). Instead of emission enhancement, we observed the Aggregation Caused Quenching (ACQ) effect. The photoluminescence quantum yield (Φ_F) of **4a** in acetonitrile is found to be 0.35, which is decreased as compared to **4a** in acetonitrile/water mixture and the Φ_F value is 0.31. This is further confirmed by single crystal X-ray structure and analysis (Fig. 3b & 3c). The phenyl units are deviated from the mean pyrazole plane with the tilt angle of 33.6° (**B**), 29.5° (**C**) and 64.1° (**D**), respectively, which clearly reflects that phenyl units are not arranged in propeller format (Fig. 3a). In addition, the crystal analysis of **4a** revealed two 1-D arrays (Fig. S27 & S28, ESI†). One of the arrays is between **B**-phenyl unit (C4-H4) and **C**-phenyl unit (π-cloud) of two molecules (Fig. S27, ESI†) and the second array is between **D**-phenyl unit (C10-H10) of one molecule with the **C**-phenyl unit (π-cloud) of neighbor molecule with the distances and angles of C4-H4…Ph(π) and C10-H10…Ph(π) are 2.88 Å, 147° and 2.88 Å, 156°, (Fig. 3c) respectively. The decrease in emission intensity upon aggregation is attributed to the intermolecular π - π stacking interaction in **4a** (Fig. S29, ESI†). The π - π distance between two closely packed molecules is 5.87 Å; however such distance in the case of **2a** and **2i** are 10.60 Å and 10.54 Å respectively (Fig. 2c and Fig. S24, ESI†). We also studied 1,3,4-triphenyl-1*H*-pyrazole[11a] and observed similar trend as in **4a** (Fig. S31, ESI†).
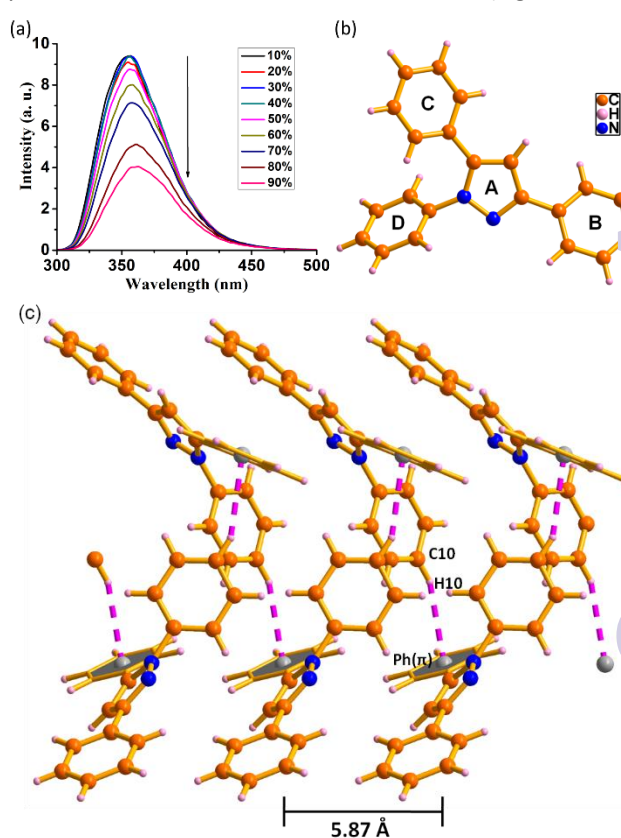

Fig. 3 (a) Emission spectra of **4a** with increasing addition of water in acetonitrile (f_w=0-90 vol%). (b) Single crystal X-ray structure of **4a**. (c) 1-D array in **4a**.

In conclusion, we have synthesized a library of tetraarylpyrazoles from commercially available starting materials by a simple and straightforward synthetic protocol. By using tetraarylpyrazoles, we have exploited the AIEE phenomenon which is hitherto unknown in the literature. We also explored that four phenyl rings were essential to demonstrate AIEE phenomenon, reduction in one of the phenyl units led to ACQ.

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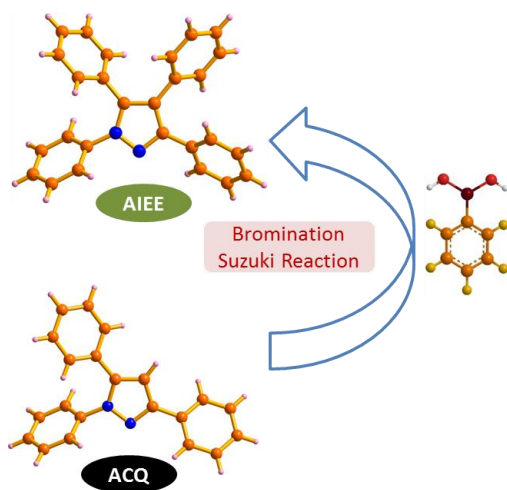
A library of tetraarylpyrazole derivatives were synthesized and explored the AIEE phenomenon.