**Electronic Supplementary Information**

**AIEE Phenomenon: Tetraaryl vs Triaryl Pyrazoles**

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EXPERIMENTAL SECTION

General Consideration

Reagents

All experiments were carried out in oven–dried glasswares under nitrogen atmosphere. 1,3-Diphenylpropan-1,3-dione, aryl and heteroaryl hydrazines were purchased from Aldrich and Acros and used as received. Pd(PPh₃)₄, aryl and heteroaryl boronic acids were purchased from Aldrich. N-Bromosuccinimide was purchase from Aldrich and recrystallized from water. Cs₂CO₃, KOH, K₂CO₃ and Et₃N were purchased from Aldrich, Acros, Merck or Alfa-Aesar and used as received. All other reagents were purchased from common suppliers and used without further purification. Flash chromatography was performed by using Merck Silica gel 60 (230–400 mesh). Reactions were monitored by thin–layer chromatography on pre-coated with silica gel 60 F254 plates (Merck & co.) and were visualized by UV. 1,3,4-triphenylpyrazole was synthesized by reported method.¹

Analytical Methods

¹H and ¹³C spectra were recorded in CDCl₃ solution using Brucker Avance DRX(400 MHz). The signals were referenced to residual chloroform (7.26 ppm, 77.16 ppm, ¹³C). Chemical shifts are reported in ppm, multiplicities are indicated by s (singlet), d (doublet), t (triplet), dd (doublet of a doublet). Gas chromatography analysis was performed on ThermoFisher ITQ 900 instrument with a FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d., 0.25 μm film thickness) using helium as carrier gas. Gas chromatography-mass analysis was carried out on ThermoFisher ITQ 900 instrument (EI) and TG-SQC capillary column using helium carrier gas. ESI HR-MS measurements were performed on Bruker micrOTOF-Q-II mass-spectrometer. The fluorescence spectra were recorded on a SPEX-Fluorolog F112X spectrofluorimeter. The electronic absorption spectra were recorded with Shimadzu 3101PC UV-Vis-NIR Scanning spectrophotometer. DLS analyses were carried out with a Zetasizer Nano S from Malvern Instruments at 25°C. The X-ray quality crystals for the compounds were grown by slow diffusion of n-hexane over CH₂Cl₂ solution. Single-crystal X-ray diffraction data of 2a, 2i and 4a were collected in a Bruker KAPPA APEX-II, four angle rotation system, Mo-Kα radiation (0.71073 Å).
Scheme 1: General Procedure for Synthesis of 1,3,5-Triaryl-1H-pyrazoles

To a solution of 1,3-diphenylpropan-1,3-dione (2.46 g, 11 mmol) in AcOH (20 mL) was added arylhydrazine (13 mmol) at room temperature. The reaction mixture was refluxed until 1,3-diketone was consumed. The reaction mixture was cooled and neutralized by saturated sodium carbonate solution. The aqueous phase was extracted with CH₂Cl₂. The combined extracts were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. Purification of the crude product by flash chromatography afforded the corresponding pyrazole as a colourless solid.

1,3,5-Triphenyl-1H-pyrazole (4a)

Yield: 2.61 g (80%) as a colourless solid.
Melting point: 130 – 132 ºC
Rᵣ: 0.31 in 5% ethyl acetate in hexane
IR (ν cm⁻¹, in KBr): 3448, 3120, 3061, 1596, 1497, 1482, 1457, 1433, 1363, 1213, 1174, 1065, 1021, 972, 957, 921, 814, 765, 700, 693, 504.

¹H NMR (400 MHz, CDCl₃): δ = 7.94 – 7.92 (m, 2H), 7.46 – 7.42 (m, 2H), 7.34 – 7.28 (m, 11H), 6.83 (s, 1H).

¹³C NMR (100 MHz, CDCl₃): δ = 152.10, 144.53, 140.26, 133.17, 130.71, 129.05, 128.88, 128.78, 128.61, 128.43, 128.13, 127.57, 125.95, 125.45, 105.34.

1-(4-Methoxyphenyl)-3,5-diphenyl-1H-pyrazole (4b)

Yield: 2.69 g (75%) as a colourless solid.
Melting point: 101 – 104 °C
Rf: 0.68 in 10% ethyl acetate in hexane

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.92$ (dd, $J = 8.3$, 1.2 Hz, 2H), 7.46 – 7.40 (m, 2H), 7.36 – 7.27 (m, 8H), 6.90 – 6.84 (m, 2H), 6.81 (s, 1H), 3.82 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 158.99, 151.77, 144.49, 133.59, 133.30, 130.75, 128.84, 128.77, 128.59, 128.32, 128.03, 126.89, 125.93, 114.25, 104.78, 55.64.

HR–MS (ESI): Calcd. for C$_{22}$H$_{18}$N$_2$O (M+H): 327.1492, found: 327.1520.

1-(4-Trifluoromethylphenyl)-3,5-diphenyl-1H-pyrazole (4c)

Yield: 3.12 g (78%) as a colourless solid.
Melting point: 113 – 115 °C
Rf: 0.51 in 2% ethyl acetate in hexane

IR (ν cm$^{-1}$, in KBr): 3064, 2372, 1611, 1523, 1509, 1484, 1458, 1410, 1364, 1325, 1168, 1159, 1125, 1108, 1075, 1057, 1016, 969, 851, 766, 697, 613.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.98 – 7.86$ (m, 2H), 7.60 (d, $J = 8.4$ Hz, 2H), 7.51 (d, $J = 8.4$ Hz, 2H), 7.45 (t, $J = 7.5$ Hz, 2H), 7.43 – 7.34 (m, 4H), 7.31 (dt, $J = 7.6$, 3.9 Hz, 2H), 6.85 (s, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 152.81, 144.74, 142.94, 132.76, 130.38, 129.05$ (q, $J = 33$ Hz), 128.92, 128.87 (2C), 128.84, 128.44, 126.14 (q, $J = 4$ Hz), 125.97, 124.91, 124.00 (q, $J = 271$ Hz), 106.39.

HR–MS (ESI): Calcd. for C$_{22}$H$_{15}$N$_2$F$_3$ (M+H): 365.1260, found: 365.1245.
1-(2-Pyridyl)-3,5-diphenyl-1H-pyrazole (4d)

Yield: 1.80 g (55%) as a colourless solid.
Melting point: 104 – 106 °C
Rf: 0.26 in 20 % ethyl acetate in hexane
IR (ν cm⁻¹, in KBr): 2373, 2345, 1580, 1469, 1362, 1329, 1074, 791, 765, 742, 699, 670, 460.

¹H NMR (400 MHz, CDCl₃): δ = 8.38 (ddd, J = 4.9, 2.0, 0.8 Hz, 1H), 7.96 – 7.93 (m, 2H), 7.77 (ddd, J = 8.0, 7.4, 2.0 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.47 – 7.41 (m, 2H), 7.39 – 7.28 (m, 6H), 7.22 (ddd, J = 7.4, 4.9, 0.8 Hz, 1H), 6.84 (s, 1H).

¹³C NMR (100 MHz, CDCl₃): δ = 152.79, 152.71, 148.61, 145.23, 138.34, 132.95, 131.20, 128.85, 128.77, 128.40, 128.37 (2C), 126.15, 122.55, 119.09, 106.57.

Scheme 2: General Procedure for Synthesis of 4–Bromo–1,3,5-triaryl-1H-pyrazoles

To a solution of 1,3,5-triarylpyrazole (8 mmol) in CCl₄ (50 mL) was added N-bromosuccinimide (1.71 g, 9.6 mmol) at room temperature. The reaction mixture was stirred at the same temperature until the pyrazole was consumed. The reaction mixture was poured into H₂O and was extracted with CH₂Cl₂. The combined extracts were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. Purification of the crude product by flash chromatography afforded the corresponding pyrazole as a colourless solid.
4-Bromo-1,3,5-triphenyl-1H-pyrazole (3a)

Yield: 2.43 g (81%) as a colourless solid.
Melting point: 224 – 226 °C
Rf: 0.35 in 5% ethyl acetate in hexane
IR (ν cm⁻¹, in KBr): 3047, 1482, 1492, 1453, 1358, 1157, 1091, 1072, 1029, 963, 769, 760, 693, 674.
¹H NMR (400 MHz, CDCl₃): δ = 8.02 – 7.99 (m, 2H), 7.50 – 7.46 (m, 2H), 7.43 – 7.38 (m, 4H), 7.36 – 7.27 (m, 7H).
¹³C NMR (100 MHz, CDCl₃): δ = 149.87, 142.15, 139.91, 132.08, 129.16, 129.12, 129.03, 128.65, 128.58, 128.50, 128.21, 127.73, 124.94, 95.04.
            377.0471, found: 377.0479.

4-Bromo-1-(4-methoxyphenyl)-3,5-diphenyl-1H-pyrazole (3b)

Yield: 3.14 g (97%) as a colourless solid.
Melting point: 109 – 110 °C
Rf: 0.36 in 20% ethyl acetate in hexane
IR (ν cm⁻¹, in KBr): 2933, 2835, 2345, 1542, 1509, 1479, 1458, 1357, 1301, 1243, 1169, 1108, 1026, 968, 837, 806, 768, 730, 699, 615, 531.
¹H NMR (400 MHz, CDCl₃): δ = 8.01 – 7.98 (m, 2H), 7.49 – 7.44 (m, 2H), 7.42 – 7.32 (m, 6H), 7.20 (dd, J = 6.8, 2.0 Hz, 2H), 6.81 (dd, J = 6.8, 2.0 Hz, 2H), 3.78 (s, 3H).
¹³C NMR (100 MHz, CDCl₃): δ = 159.02, 149.50, 142.15, 133.22, 132.21, 130.36, 129.19, 129.03, 128.59, 128.47 (2C), 128.19, 126.41, 114.16, 94.42, 55.60.
HR-MS (ESI): Calcd. for C₂₂H₁₇N₂OBr (M+H): 405.0471, found: 405.0552.
            407.0451, found: 407.0533.

ESI - 6
4-Bromo-1-(4-trifluoromethylphenyl)-3,5-diphenyl-1H-pyrazole (3c)

Yield: 3.44 g (97%) as a colourless solid.
Melting point: 104 –106 °C
Rf: 0.51 in 20 % ethyl acetate in hexane
IR (ν cm⁻¹, in KBr): 3448, 2372, 2345, 1701, 1324, 1167, 1121, 1065, 842, 765, 695, 460.
¹H NMR (400 MHz, CDCl₃): δ = 8.03 – 8.00 (m, 2H), 7.57 (d, J = 8.8 Hz, 2H), 7.52 – 7.48 (m, 2H), 7.47 – 7.42 (m, 6H), 7.38 – 7.34 (m, 2H).
¹³C NMR (100 MHz, CDCl₃): δ = 150.66, 142.57, 142.40, 131.74, 130.29, 129.61, 129.36 (q, J = 33 Hz), 128.99, 128.88, 128.86, 128.59, 128.21, 126.22 (q, J = 4 Hz), 123.88 (q, J = 270 Hz), 124.48, 96.29.
375.0346, found: 375.0364.

4-Bromo-1-(2-pyridyl)-3,5-diphenyl-1H-pyrazole (3d)

Yield: 2.86 g (95%) as a colourless solid.
Melting point: 121 °C
Rf: 0.28 in 20 % ethyl acetate in hexane
IR (ν cm⁻¹, in KBr): 3056, 1590, 1483, 1471, 1360, 1313, 1161, 1143, 1087, 1074, 1030, 995, 980, 967, 925, 771, 706, 697, 617, 512, 463.
¹H NMR (400 MHz, CDCl₃): δ = 8.32 (ddd, J = 4.8, 2.0, 0.8 Hz, 1H), 8.04 – 8.01 (m, 2H), 7.74 (ddd, J = 8.1, 7.4, 2.0 Hz, 1H), 7.53 (dt, J = 8.0, 0.8 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.44 – 7.34 (m, 6H), 7.20 (ddd, J = 7.4, 4.8, 0.8 Hz, 1H).
¹³C NMR (100 MHz, CDCl₃): δ = 152.27, 150.60, 148.57, 142.70, 138.37, 131.92, 130.17, 129.74, 128.94, 128.77, 128.47, 128.39 (2C), 122.76, 118.58, 96.45.
378.0424, found: 378.0079.
Scheme 3: Optimization of Cross-coupling of 4-Bromo-1,3,5-triphenyl-1H-pyrazole with Phenyl boronic Acid

Table 1: Standardization of Cross-coupling Reaction

<table>
<thead>
<tr>
<th>S. No</th>
<th>Base</th>
<th>Solvent</th>
<th>Catalyst</th>
<th>Product 2a</th>
<th>Product 4a</th>
<th>Product 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na₂CO₃ (2M)</td>
<td>iPrOH</td>
<td>Pd(PPh₃)₄</td>
<td>11%</td>
<td>36%</td>
<td>20%</td>
</tr>
<tr>
<td>2</td>
<td>Na₂CO₃ (2M)</td>
<td>iPrOH</td>
<td>Pd(dba)₂</td>
<td>-</td>
<td>70%</td>
<td>15%</td>
</tr>
<tr>
<td>3</td>
<td>Ba(OH)₂ (2M)</td>
<td>Toluene</td>
<td>Pd(PPh₃)₄</td>
<td>38%</td>
<td>17%</td>
<td>5%</td>
</tr>
<tr>
<td>4</td>
<td>Cs₂CO₃</td>
<td>Toluene</td>
<td>Pd(PPh₃)₄</td>
<td>38%</td>
<td>17%</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>Cs₂CO₃</td>
<td>THF</td>
<td>Pd(PPh₃)₄</td>
<td>38%</td>
<td>17%</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>Cs₂CO₃</td>
<td>Toluene</td>
<td>Pd(PPh₃)₄</td>
<td>16%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7ᵇ</td>
<td>Cs₂CO₃</td>
<td>THF</td>
<td>Pd(PPh₃)₄</td>
<td>64%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7ᵇ,ᶜ</td>
<td>Cs₂CO₃</td>
<td>THF</td>
<td>Pd(PPh₃)₄</td>
<td>75%</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*Reaction Conditions: 4-Bromopyrazole (0.5 mmol), Phenyl Boronic Acid (0.6 mmol), Catalyst (5 mol-%), Base (1.5 mmol), Solvent (2 mL), 80 °C, 12 h; Reaction was performed in Sealed tube; Reaction time was 16 h.

Scheme 4: General Procedure for Synthesis of 1,3,4,5-Tetraaryl-1H-pyrazoles by Suzuki Reaction

An oven-dried sealed tube was charged with Pd(PPh₃)₄ (5-15 mol%), 4-bromo-1,3,5-triarylpyrazole (0.45 mmol), arylboronic acid (0.54 mmol) and Cs₂CO₃ (0.67 mmol) in THF (5 mL) and was stirred at 80°C. The reaction was monitored by TLC or GC/MS analysis. After the
starting material was completely consumed, the reaction mixture was then cooled to room temperature and was purified by flash chromatography.

1,3,4,5-Tetraphenyl-1H-pyrazole (2a)

Yield: 0.126 g (75%) as a colourless solid.
Melting point: 202°C
Rf: 0.47 in 20% ethyl acetate in hexane
UV (λ_{max}): 240 nm (15 μM solution in CH₃CN)
IR (ν cm⁻¹, in KBr): 2925, 2854, 2372, 2345, 1594, 1496, 1458, 1362, 1074, 964, 921, 793, 746, 768, 700, 650.

¹H NMR (400 MHz, CDCl₃): δ = 7.54 – 7.52 (m, 2H), 7.36 – 7.28 (m, 8H), 7.24 – 7.18 (m, 6H), 7.13 – 7.10 (m, 2H), 7.08 – 7.05 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ = 150.30, 141.54, 140.0, 133.21, 133.19, 133.16, 130.84, 130.56, 130.17, 128.89, 128.54, 128.39, 128.32, 128.29, 127.78, 127.37, 126.80, 125.47, 120.85.


4-(4-Methoxyphenyl)-1,3,5-triphenyl-1H-pyrazole (2b)

Yield: 0.116 g (64%) as a colourless solid.
Melting point: 138°C
Rf: 0.26 in 5% ethyl acetate in hexane
IR (ν cm⁻¹, in KBr): 3050, 3003, 2926, 1595, 1553, 1508, 1496, 1361, 1246, 1174, 1028, 969, 837, 770, 760, 700.

¹H NMR (400 MHz, CDCl₃): 7.76 – 7.54 (m, 2H), 7.32 – 7.20 (m, 11H), 7.08 – 7.05 (m, 2H), 7.03 – 7.01 (m, 2H), 6.76 (d, J = 8.4 Hz, 2H), 3.78 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ = 158.50, 150.29, 141.41, 140.09, 133.31, 131.88, 130.57, 130.30, 128.88, 128.50, 128.39, 128.32, 128.21, 127.72, 127.32, 125.45, 125.40, 120.47, 113.83, 55.23.

4-(2-Methoxyphenyl)-1,3,5-triphenyl-1H-pyrazole (2c)

Yield: 0.132 g (73%) as a colourless solid.
Melting point: 116 °C
Rf: 0.23 in 20 % ethyl acetate in hexane
IR (ν cm⁻¹, in KBr): 2373, 2345, 1593, 1495, 1364, 1273, 1249, 1179, 1113, 1074, 1024, 970, 791, 763, 733, 699, 670.

¹H NMR (400 MHz, CDCl₃): δ = 7.54 – 7.52 (m, 2H), 7.35 – 7.34 (m, 2H), 7.30 – 7.28 (m, 2H), 7.27 – 7.22 (m, 5H), 7.20 – 7.14 (m, 3H), 7.06 – 7.01 (m, 3H), 6.84–6.81 (m, 2H), 3.36 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ = 157.65, 150.76, 141.98, 140.18, 133.91, 132.79, 130.78, 129.95, 128.83(2C), 128.18, 128.17, 127.99, 127.66, 127.54, 127.17, 125.41, 122.47, 120.69, 117.10, 111.33, 55.11.

HR–MS (ESI): Calcd. for C₂₈H₂₂N₂O (M+H): 403.1805, found: 403.1777.

4-(4-Formylphenyl)-1,3,5-triphenyl-1H-pyrazole (2d)

Yield: 0.067 g (37%) as a colourless solid.
Melting point: 147–148 °C
Rf: 0.44 in 25 % ethyl acetate in hexane
IR (ν cm⁻¹, in KBr): 2925, 2373, 2345, 1718, 1700, 1604, 1496, 1363, 1212, 1172, 1062, 970, 835, 769, 697.

¹H NMR (400 MHz, CDCl₃): δ = 9.96 (s, 1H), 7.71 (d, J = 8.4 Hz, 2H), 7.49 – 7.47 (m, 2H), 7.31 – 7.29 (m, 9H), 7.25 – 7.21 (m, 4H), 7.06–7.05 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ = 192.10, 150.54, 141.96, 140.05, 139.73, 134.71, 132.73, 131.25, 130.52, 129.76, 129.69, 128.99, 128.76, 128.73, 128.70, 128.55, 128.18, 127.68, 125.51, 119.59.

1-(4-Methoxyphenyl)-3,4,5-triphenyl-1H-pyrazole (2e)

Yield: 0.127 mg (70%) as a colourless solid.
Melting point: 186 °C
Rf: 0.32 in 20% ethyl acetate in hexane
IR (ν cm⁻¹, in KBr): 3807, 2931, 2372, 2345, 1542, 1512, 1298, 1253, 1167, 1066, 1032, 969, 834, 771, 724, 699, 614, 540, 463.
¹H NMR (400 MHz, CDCl₃): δ = 7.53 – 7.51 (m, 2H), 7.29 – 7.18 (m, 11H), 7.12 – 7.09 (m, 2H), 7.05 (dd, J = 8.2, 1.6 Hz, 2H), 6.85 – 6.81 (m, 2H), 3.80 (s, 3H).
¹³C NMR (100 MHz, CDCl₃): δ = 158.79, 149.96, 141.51, 133.39, 133.37 (2C), 130.85, 130.59, 130.25, 128.54, 128.35, 128.31 (2C), 128.16, 127.67, 126.86, 126.71, 120.39, 114.08, 55.60.

1,4-Di(4-methoxyphenyl)-3,5-diphenyl-1H-pyrazole (2f)

Yield: 0.136 mg (70%) as a colourless solid.
Melting point: 187–188 °C
Rf: 0.26 in 20% ethyl acetate in hexane
IR (ν cm⁻¹, in KBr): 3456, 2932, 1546, 1515, 1458, 1370, 1291, 1250, 1171, 1035, 971, 838, 771, 702, 680.
¹H NMR (400 MHz, CDCl₃): δ = 7.55 – 7.53 (m, 2H), 7.31 – 7.24 (m, 4H), 7.22–7.17 (m, 4H), 7.05 (dd, J = 8.0, 2.0 Hz, 2H), 7.03 – 6.99 (m, 2H), 6.85 – 6.79 (m, 2H), 6.77 – 6.73 (m, 2H), 3.79 (s, 3H), 3.77 (s, 3H).
¹³C NMR (100 MHz, CDCl₃): δ = 158.8, 158.47, 149.82, 141.46, 133.28, 133.25, 131.87, 130.58, 130.26, 128.51, 128.35, 128.31, 128.12, 127.68, 126.88, 125.47, 120.00, 114.08, 113.83, 55.59, 55.23.
1-(4-Trifluoromethylphenyl)-3,4,5-triphenyl-1H-pyrazole (2g)

Yield: 0.135 mg (68%) as a colourless solid.

Melting point: 175 °C

Rf: 0.34 in 4% ether in hexane

IR (ν cm⁻¹, in KBr): 3057, 2372, 2345, 1609, 1522, 1437, 1366, 1327, 1162, 1123, 1106, 1073, 1058, 1018, 967, 846, 776, 797, 766, 735, 726, 697, 684, 662, 593.

¹H NMR (400 MHz, CDCl₃): δ = 7.57 (d, J = 8.4 Hz, 2H), 7.56 – 7.48 (m, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.33 – 7.28 (m, 5H), 7.24 – 7.20 (m, 4H), 7.11 – 7.08 (m, 4H).

¹³C NMR (100 MHz, CDCl₃): δ = 151.15, 142.80, 141.66, 132.84, 132.74, 130.76, 130.49, 129.86, 128.93 (q, J = 33 Hz), 128.73 (2C), 128.48, 128.41, 128.38, 128.07, 127.04, 126.07 (q, J = 4 Hz), 124.93, 124.01 (q, J = 270 Hz), 121.83.

HR–MS (ESI): Calcd. for C₂₈H₁₉F₃N₂ (M+H): 441.1573, found: 441.1513.

1-(2-Pyridyl)-3,4,5-triphenyl-1H-pyrazole (2i)

Yield: 0.114 mg (68%) as a colourless solid (15 mol% of catalyst).

Melting point: 174 °C

Rf: 0.34 in 50% ether in hexane

IR (ν cm⁻¹, in KBr): 2372, 2345, 1586, 1458, 1470, 1449, 1361, 1179, 1146, 1074, 991, 971, 800, 787, 770, 742, 701, 651.

¹H NMR (400 MHz, CDCl₃): δ = 8.35 (ddd, J = 5.0, 1.6, 0.8 Hz, 1H), 7.75 – 7.71 (m, 1H), 7.54 – 7.51 (m, 3H), 7.29 – 7.27 (m, 3H), 7.23 – 7.18 (m, 7H), 7.14 – 7.07 (m, 4H).

¹³C NMR (100 MHz, CDCl₃): δ = 152.58, 151.19, 148.63, 141.92, 138.19, 133.07, 133.01, 130.89, 130.59, 130.39, 128.62, 128.31, 128.27, 128.15, 128.11, 127.92, 126.92, 122.46, 121.81, 119.28.

4-(2-Fluoro-3-pyridyl)-1,3,5-triphenyl-1H-pyrazole (2h)

Yield: 0.132 g (75%) as a colourless solid (15 mol% of catalyst).

Melting point: 225 °C

Rf: 0.25 in 20 % ethyl acetate in hexane

IR (ν cm⁻¹, in KBr): 3448, 2925, 2372, 2345, 1498, 1426, 1365, 1246, 1211, 1111, 1073, 102, 971, 844, 809, 790, 767, 738, 700, 670.

¹H NMR (400 MHz, CDCl₃): δ = 8.14 (d, J = 4.4 Hz, 1H), 7.55 – 7.48 (m, 3H), 7.36 – 7.27 (m, 9H), 7.24 – 7.20 (m, 2H), 7.10 – 7.06 (m, 3H).

¹³C NMR (100 MHz, CDCl₃): δ = 161.43 (d, J = 239.0 Hz), 150.84, 146.89 (d, J = 14 Hz), 143.57 (d, J = 5.0 Hz), 142.86, 139.75, 132.77, 129.93, 129.57, 128.98, 128.77, 128.66, 128.61, 128.18, 127.86, 127.66, 125.36, 121.38 (d, J = 5.0 Hz), 116.51 (d, J = 31. Hz), 112.73 (d, J = 4.0 Hz).


References:

Figure S1: Absorption (a) and emission (b) spectrum of 2a in acetonitrile.

Figure S2: (a) Emission spectra of 2a in acetonitrile/water mixtures with increasing addition of water ($f_w = 0$-$90$ vol%). (b) The changes in the emission intensity of 2a with the water contents in the acetonitrile/water mixture.
Figure S3: Absorption spectra of 2a in acetonitrile ($f_w = 0$ vol%) and acetonitrile/water mixture ($f_w = 90$ vol%)

Figure S4: Temperature effect on the emission intensity of 2a in acetonitrile/water (1:9 v/v), ($\lambda_{ex} = 280$ nm)
Figure S5: Absorption (a) and emission (b) spectrum of 2e in acetonitrile.

Figure S6: (a) Emission spectra of 2e in acetonitrile/water mixtures with increasing addition of water ($f_w=0-90$ vol%). (b) The changes in the emission intensity of 2e with the water contents in the acetonitrile/water mixture.
**Figure S7:** Absorption spectra of 2e in acetonitrile ($f_w = 0$ vol%) and acetonitrile/water mixture ($f_w = 90$ vol%)

**Figure S8:** Temperature effect on the emission intensity of 2e in acetonitrile/water (1:9 v/v), ($\lambda_{ex}=280$ nm)
**Figure S9:** Absorption (a) and emission (b) spectrum of 2i in acetonitrile.

**Figure S10:** (a) Emission spectra of 2i in acetonitrile/water mixtures with increasing addition of water ($f_w=0$-95 vol%). (b) The changes in the emission intensity of 2i with the water contents in the acetonitrile/water mixture.
**Figure S11**: Absorption spectra of 2i in acetonitrile ($f_w = 0$ vol%) and acetonitrile/water mixture ($f_w = 90$ vol%)

**Figure S12**: Temperature effect on the emission intensity of 2i in acetonitrile/water (1:9 v/v), ($\lambda_{ex}=280$ nm)
Figure S13: Single crystal X-ray structure of 2a with the dihedral angle between the planes.

Figure S14: 1-D array in 2a. The array is formed between one of the phenyl-CHs (C7-H7; C25-H25) with two different units of pyrazole nitrogens (N2) with the bond distances and angles of C7-H7…N2 and C25-H25…N2 are 2.78 Å; 141° and 2.80Å; 140°.
**Figure S15**: 1-D array in 2a. The array is formed between one of the phenyl-CHs (C6-H6) and N-phenyl-CH (C26-H26) unit with two different phenyl π-clouds with the bond distances and angles of C6-H6...Ph(π) and C26-H26...Ph(π) are: 3.00 Å and 144°.

**Figure S16**: 2-D array in 2a. The π – π distance between two closely packed molecules is 10.60Å. The bond distance and angles of C7-H7...N2; C25-H25...N2; C6-H6...Ph(π) and C26-H26...Ph(π) are 2.78 Å & 141°; 2.80Å & 140° and 3.00 Å &144°.
**Figure S17:** Crystal packing in 2a.

**Figure S18:** The π – π distance between two closely packed molecules in 2a is 10.60 Å.
Figure S19: Single crystal X-ray structure of 2i with the dihedral angle between the planes.

Figure S20: 1-D array in 2i. The array is formed between one of the phenyl-CHs (C7-H7; C25-H25) with two different units of pyrazole nitrogens (N2) with the bond distances and angles of C7-H7…N2 and C25-H25…N2 are 2.66 Å; 133° and 2.70Å; 145°.
**Figure S21**: 1-D array in 2i. The array is formed between one of the phenyl-CHs (C6-H6) and N-phenyl-CH (C26-H26) unit with two different phenyl π-clouds with the bond distances and angles of C6-H6…Ph(π) and C26-H26…Ph(π) are 3.05 Å; 144° and 2.92 Å; 145°.

**Figure S22**: 2-D array in 2i. The π – π distance between two closely packed molecules is 10.54Å. The bond distances and angles of C7-H7…N2; C25-H25…N2; C6-H6…Ph(π) and C26-H26…Ph(π) are 2.66 Å & 133°; 2.70Å & 145°; 3.05 Å &144° and 2.92 Å & 145°.
**Figure S23**: Crystal packing in 2a.

**Figure S24**: The $\pi - \pi$ distance between two closely packed molecules in 2i is 10.54 Å.
**Figure S25:** a) Emission spectra of 4a in acetonitrile, b) Emission spectra of 4a in acetonitrile /water mixtures with increasing addition of water ($f_w = 0$-90 vol%).

**Figure S26:** Single crystal X-ray structure of 4a with the dihedral angle between the planes.

Dihedral Angle (°) between Planes

- A and B: 33.6°
- A and C: 29.5°
- A and D: 64.1°
**Figure S27** 1-D array in 4a. The array is formed between one of the phenyl-CHs (C4-H4) and second pyrazole unit phenyl π-cloud with the bond distance and angle of C4-H4…Ph(π) is: 2.88 Å and 147°.

**Figure S28** 1-D array in 4a. The array is formed between one of the pyrazole N-phenyl-CHs (C10-H10) and second pyrazole unit phenyl π-cloud with the bond distance and angle of C10-H10…Ph(π) is: 2.88 Å and 156°. The π – π distance between two closely packed molecules is 5.87 Å.
Figure S29: Crystal packing in 4a.

Figure S30: The π – π distance between two closely packed molecules in 4a is 5.87 Å.
Crystallographic data of 2a, 2i and 4a:

Crystallographic data of 2a in CH$_2$Cl$_2$/n-hexane: C$_{27}$H$_{20}$N$_2$, Mw = 372.45, monoclinic, space group P2$_1$, a = 9.9297(3) Å, b = 9.6354(3) Å, c = 10.6037(3) Å, α = 90.00 °, β = 90.080(2) °, γ = 90.00°, V = 1014.53(5) Å$^3$, Z = 2, D$c$alc = 1.219 mg/m$^3$, T = 296(2) K, R1 = 0.0443 {I > 2σ (I)}, R2w = 0.1085, GOF = 1.038.

Crystallographic data of 2i in CH$_2$Cl$_2$/n-hexane: C$_{26}$H$_{19}$N$_3$, Mw = 373.44, monoclinic, space group P2$_1$, a = 9.7331(3) Å, b = 9.7771(3) Å, c = 10.5392(3) Å, α = 90.00 °, β = 90.204(2) °, γ = 90.00°, V = 1002.92(5) Å$^3$, Z = 2, D$c$alc = 1.237 mg/m$^3$, T = 296(2) K, R1 = 0.0431 {I > 2σ (I)}, R2w = 0.1021, GOF = 1.002.

Crystallographic data of 4a in CH$_2$Cl$_2$/n-hexane: C$_{21}$H$_{16}$N, Mw = 296.36, orthorhombic, space group Fdd2, a = 29.627(10) Å, b = 36.790(12) Å, c = 5.865(2) Å, α = 90.00 °, β = 90.00 °, γ = 90.00°, V = 6393(6) Å$^3$, Z = 16, D$c$alc = 1.232 mg/m$^3$, T = 296(2) K, R1 = 0.0401 {I > 2σ (I)}, R2w = 0.0992, GOF = 0.978.

CCDC-1032189, 1032190 & 1032191 contain the supplementary crystallographic data for 2a, 2i and 4a. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
Figure S31: (a) Emission spectra of 1,3,4-triphenyl-1H-pyrazole (5a) in acetonitrile/water mixtures with increasing addition of water ($f_w$=0-90 vol%).
$^1$H NMR Spectra of 4a

$^{13}$C NMR Spectra of 4a
$^1$H NMR Spectra of 4b

$^{13}$C NMR Spectra of 4b
$^{1}$H NMR Spectra of 4c

$^{13}$C NMR Spectra of 4c
$^1$H NMR Spectra of 4d

$^{13}$C NMR Spectra of 4d
$^1$H NMR Spectra of 3a

$^{13}$C NMR Spectra of 3a
$^1$H NMR Spectra of 3b

$^{13}$C NMR Spectra of 3b

ESI - 36
$^1$H NMR Spectra of 3d

$^{13}$C NMR Spectra of 3d
\( ^1H \) NMR Spectra of 2a

\( ^13C \) NMR Spectra of 2a

ESI - 39
$^{1}$H NMR Spectra of 2b

$^{13}$C NMR Spectra of 2b

ESI - 40
$^1$H NMR Spectra of 2c

$^{13}$C NMR Spectra of 2c

ESI - 41
$^{1}H$ NMR Spectra of 2d

$^{13}C$ NMR Spectra of 2d
$^1$H NMR Spectra of 2e

$^{13}$C NMR Spectra of 2e
$^1$H NMR Spectra of 2f

$^{13}$C NMR Spectra of 2f
$^{1}H$ NMR Spectra of 2g

$^{13}C$ NMR Spectra of 2g
$^1$H NMR Spectra of 2i

$^{13}$C NMR Spectra of 2i
$^{1}$H NMR Spectra of 2h

$^{13}$C NMR Spectra of 2h