Supporting Information

Aggregation induced emission (AIE) active N-arylated ferrocenyl pyrazole chromophores: second order nonlinear optical and turn on/off fluorescence for detection of picric acid in mixed aqueous media

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1. Determination of the Quantum Yield

The photoluminescence quantum yields (Φ) values of chromophores in degassed CH₃CN/H₂O solutions were measured referenced to Quinine Sulphate ($\Phi_{st} = 0.54$ in 0.1M H₂SO₄)¹ by using the following equation (1):

$$\Phi_x = \Phi_{st} \times \left[\frac{A_{st}}{A_x}\right] \times \left[\frac{I_x}{I_{st}}\right] \times \left[\frac{\eta_x^2}{\eta_{st}^2}\right]$$
(1)

Subscripts "x" and "st" stands for unknown and standard (Quinine Sulphate) sample, respectively; Φ for quantum yield, A for absorbance, η for the refractive index of the solvents, I is the area under the fluorescence spectra on an energy scale.

2. Preparation of Fluorometric Titration Solutions

The sensing experiments were carried out by monitoring the fluorescence quenching behaviour of the AIE-active compounds 1 and 3 in CH₃CN/water mixtures (fw = 80 vol%) and 2 and 4 in CH₃CN/water mixtures (fw = 90 vol%). The interaction of N-arylated ferrocenyl pyrazole chromophores with nitroaromatics was studied by adding an appropriate volume of 10 µM aqueous solutions of picric acid (PA) in gradually increasing amount. For each addition, at least three fluorescence spectrums were recorded repeatedly at 298K to obtain concordant value. The fluorescence spectra of the resultant mixtures were then recorded immediately at room temperature with an excitation wavelength of 365 nm, and the emission data were collected in the wavelength range of 400–550 nm.

3. Calculation of Stern-Volmer Fluorescence Quenching (%) Constant

The Stern–Volmer relationship establishes the correlation of intensity changes with the quencher concentration [Q] was calculated using the equation (2) as follows:

$$\frac{I_0}{I} = 1 + K_{SV} [Q]$$
 (2)

Where I_0 is the initial intensity of the sensors and I is the intensity after addition of a fixed volume of analytes. Stern-Volmer constants (*K*_{SV}) were obtained for all the cases, I_0/I vs [PA] plot is linear when the concentration of PA is low.

4. Detection Limit

The detection limit was calculated based on the fluorescence titration. The emission spectrum of N-arylated ferrocenyl pyrazole as a function of its increasing concentration was measured five times, and the standard deviation of blank measurement was achieved. To gain the slope, the ratio of emission intensity at 435 nm in (1:8 and 1:9 v/v) CH₃CN/water was plotted against the concentration of PA. The detection limit was calculated using the following equation (3).²

Detection limit =
$$\frac{3\sigma}{K}$$
 (3)

Where σ is the standard deviation of blank measurement, and K = slope of the plot between the ratio of emission intensity versus [PA].

5. Chan-Lam C-N cross coupling mechanism for synthesis of N-arylated ferrocenyl pyrazole

Initially, the ligand exchange of copper(II) acetate with pyrazole with the aid of a base forms the intermediate 'a' followed by transmetallation of aryl boronic acid-producing the Cu(II) complex 'b'; then reductive elimination of the Cu(II) complex delivers the target products and copper(0) species (Scheme S1). Simultaneously, the oxidation of Cu(II) complex in the presence of ambient oxygen is also possible, generating the copper(III) species which provides the products and copper(I) by reductive elimination. Finally, the copper(0) or copper(I) species could be oxidized to the active copper(II) species if the coupling proceeds through a catalytic manner.³⁻⁴



Scheme S1. The reaction mechanism for the synthesis of N-arylated ferrocenyl pyrazoles 1-4.6. FT-IR Spectral Studies

The N-arylated ferrocenyl pyrazole was characterized by FT-IR spectroscopy and the obtained spectra are shown in Fig.. S1. The weak bands observed at 3118-3050 cm⁻¹ for all the compounds are attributed to the aromatic v(C–H) vibrations. Apart from these, strong characteristic bands at 1600-1570 cm⁻¹ and 1550-1510 cm⁻¹ for the compounds confirmed the presence of v(C=C) and v(C=N) indicate that the presence of the pyrazole core appeared. Furthermore, the absorption medium band is at 1010-1030 cm⁻¹ due to v(N–N) in all the pyrazole derivatives. The C–H bending mode of the ferrocene ring was observed the band at 800-850 cm⁻¹ for all the compounds.⁵



Fig. S1 FT-IR spectra of N-arylated ferrocenyl pyrazoles 1-4.

7. Solid-State UV-Vis Spectra (DRS)

UV-Vis-NIR diffuse reflectance spectra of N-arylated ferrocenyl pyrazole 1-4 exhibits strong absorption in the visible light region at the transfer of charge involving the transition with maximum absorption at 541 (1), 558 (2), 558 (3) and 541(4) nm is due to the contribution of LMCT band, the compound is from 300–900 nm which proves that there is an absorption in most of the visible region (Fig. S2). The cut-off wavelengths observed are found to vary from sample to sample and are the lowest for the sample at N-arylated ferrocene pyrazole.

$$(\alpha h\nu)^2 = A(h\nu - E_g) \tag{2}$$

The relation between the absorption coefficient (α) was calculated using the Kubelka– Munk equation⁶ and the incident photon energy ($h\nu$) can be determined by using Tauc's relationship.⁷ To experimentally determine the optical energy gap, E_g of the investigated N-arylated ferrocene pyrazole, one can plot ($\alpha h\nu$)² vs the photon energy ($h\nu$) using the optical absorption data, as shown in (Fig. S3). The optical band gap at 4.09 (1), 3.60 (2), 3.38 (3) and 2.72 (4) eV, for these band gap can be effectively modulated by varying the substituents without changing the ferrocene pyrazole moiety.



Fig. S2 DRS-UV-Vis absorption spectra of N-arylated ferrocenyl pyrazoles 1-4.



Fig. S3 Plots of $(\alpha h\nu)^2$ versus photon energy h ν for N-arylated ferrocenyl pyrazoles 1-4.



Fig. S4 ¹H NMR spectrum of N-arylated ferrocenyl pyrazole 1 in CDCl₃.



Fig. S5 ¹³C NMR spectrum of N-arylated ferrocenyl pyrazole 1 in CDCl₃.



Fig. S6¹⁹F NMR spectrum of N-arylated ferrocenyl pyrazole 1 in CDCl₃.



Fig. S7 ¹H NMR spectrum of N-arylated ferrocenyl pyrazole 2 in CDCl₃.



Fig. S8 ¹³C NMR spectrum of N-arylated ferrocenyl pyrazole 2 in CDCl₃.



Fig. S9 ¹⁹F NMR spectrum of N-arylated ferrocenyl pyrazole 2 in CDCl₃.



Fig. S10 ¹H NMR spectrum of N-arylated ferrocenyl pyrazole 3 in CDCl₃.



Fig. S11¹³C NMR spectrum of N-arylated ferrocenyl pyrazole 3 in CDCl₃.



Fig. S12¹⁹F NMR spectrum of N-arylated ferrocenyl pyrazole 3 in CDCl_{3.}



Fig. S13 ¹H NMR spectrum of N-arylated ferrocenyl pyrazole 4 in CDCl₃.



Fig. S14 ¹³C NMR spectrum of N-arylated ferrocenyl pyrazole 4 in CDCl₃.



Fig. S15¹⁹F NMR spectrum of N-arylated ferrocenyl pyrazole 4 in CDCl_{3.}



Fig. S16 GC-Mass spectrum of N-arylated ferrocenyl pyrazole 1.



Fig. S17 GC-Mass spectrum of N-arylated ferrocenyl pyrazole 2.



Fig. S18 GC-Mass spectrum of N-arylated ferrocenyl pyrazole 3.



Fig. S19 GC-Mass spectrum of N-arylated ferrocenyl pyrazole 4.



Fig. S20 The planarity of the N-arylated ferrocenyl pyrazole molecules 2-4 (measured by its torsion or dihedral angle Φ between ferrocene and pyrazole ring).

Fig. S21 Crystal-Packing diagram for N-arylated ferrocenyl pyrazoles 2-4.

Fig. S22 The π - π stacking interactions in N-arylated ferrocenyl pyrazoles 2-4.

Fig. S23 Optimized structure of N-arylated ferrocenyl pyrazoles 1-4 calculated at B3LYP/6- $31+G^{**}$ basis set.

Fig. S24 UV–Vis absorption spectra of N-arylated ferrocenyl pyrazoles 1-4 in CH₃CN solution $(1 \times 10^{-5} \text{ M})$.

Fig. S25 UV-Vis absorption spectra of the N-arylated ferrocenyl pyrazole 2 in various polarity solvents (1×10^{-5} M).

Fig. S26 UV-Vis absorption spectra of the N-arylated ferrocenyl pyrazole 3 in various polarity solvents (1×10^{-5} M).

Fig. S27 UV-Vis absorption spectra of the N-arylated ferrocenyl pyrazole 4 in various polarity solvents (1×10^{-5} M).

Fig. S28 The UV-Visible spectra of N–arylated ferrocenyl pyrazole 1-4 (Insets: different CH₃CN/water fractions (*fw*) at a concentration of 1×10^{-4} M).

Fig. S29 The emission spectra of N–arylated ferrocenyl pyrazoles 1-4 in CH₃CN solution $(1 \times 10^{-5} \text{ M})$.

Fig. S30 The PL spectra of N–arylated ferrocenyl pyrazole **2** (Insets: different water fractions (*fw*) at a concentration of 1×10^{-5} M).

Fig. S31 The PL spectra of N–arylated ferrocenyl pyrazole **3** (Insets: different water fractions (*fw*) at a concentration of 1×10^{-5} M).

Fig. S32 The PL spectra of N–arylated ferrocenyl pyrazole **4** (Insets: different water fractions (*fw*) at a concentration of 1×10^{-5} M).

Fig. S33 The UV-vis absorption spectra titration of N-arylated ferrocenyl pyrazoles 1-4 at a concentration of 1×10^{-6} M CH₃CN/water mixture with the addition of different concentrations of PA in CH₃CN solution.

Fig. S34 Cyclic voltammetry of N-arylated ferrocenyl pyrazole 1-4 with different nitroaromatics for with and without AIE state.

Fig. S35 Histogram of $(I_o-I)/I$ for compound 1, where I_o and I equal the max intensity of PL spectra at quenching substrate.

Fig. S36 The stern-Volmer plot of I₀/I *versus* picric acid concentrations of the suspension in aqueous solution for N–arylated ferrocenyl pyrazoles 1-4.

Fig. S37 Benesi-Hildebrand plot for N-arylated ferrocenyl pyrazoles 1-4 response to picric acid.

Fig. S38 The calibration plot of picric acid with a limit of detection for N–arylated ferrocenyl pyrazoles 1-4.

Fig. S39 HR-TEM images of AIE-aggregates for N-arylated ferrocenyl pyrazoles **2-4** at 0%, 80% and 90% of water fraction.

Identification code	CF ₃ (2)	CN (3)	NO ₂ (4)
CCDC No.	1530715	1456686	1530713
Empirical formula	$C_{21}H_{14}F_6FeN_2 \\$	$C_{21}H_{14}F_3FeN_3$	$C_{20}H_{14}F_3FeN_3O_2$
Formula weight	464.19	421.20	441.19
Temperature K	296(2) K	296(2) K	296(2) K
Wavelength Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_{1}/c$	$P\overline{1}$	$P2_{1}/n$
a, Å	12.1430(9)	9.6659(8)	10.0460(7)
b, Å	10.9621(9)	10.9560(12)	19.2919(16)
c, Å	15.5642(14)	10.9885(9)	10.2577(8)
$\alpha,^{\circ}$	90°	101.657(4)°	90°
$\beta,^{\circ}$	112.394(4)°	115.548(3)°	109.768(5)°
γ,°	90°	107.868(4)°	90°
Volume Å ³	1915.6(3)	920.39(15)	1870.9(2)
Z	4	2	4
Density (calculated) Mg/m ³	1.610	1.520	1.566
Absorption coefficient mm ⁻¹	0.854	0.859	0.857
F(000)	936	428	896
Crystal size	0.30 x 0.20 x 0.20	0.35 x 0.30 x 0.30	0.35 x 0.30 x 0.30
Theta range for data collection°	3.27 to 28.35°	2.12 to 28.19°	2.11 to 28.33°
Reflections collected / unique	15188 / 4754	7386 / 4369	14748 / 4639
Data / restraints / parameters	4754 / 0 / 271	4369 / 0 / 253	4639 / 0 / 262
Goodness-of-fit on F2	1.042	0.830	1.026
Final R indices [I>2o(I)]	R1 = 0.0521,	R1 = 0.0549,	R1 = 0.0568,
R indices (all data)	wR2 = 0.1443 R1 = 0.0683, wR2 = 0.1592	wR2 = 0.1813 R1 = 0.0780, wR2 = 0.2189	wR2 = 0.1497 R1 = 0.0983, wR2 = 0.1786

Table S1. Crystal data and structure refinement parameters for N-arylated ferrocenyl pyrazoles2-4

	CF ₃ (2)	CN (3)	NO ₂ (4)			
Average Fe-C	2.039	2.038	2.033			
Fe-Cent(1)	1.643	1.645	1.643			
Fe-Cent(2)	1.651	1.655	1.651			
Cent(1)-Fe(1)-Cent(2)	177.05	178.65	179.35			
N-N	1.361(3)	1.366(4)	1.365(4)			
N-C	1.430(3)	1.426(4)	1.421(4)			
N(1)-C(7)	1.364(4)	1.364(4)	1.363(4)			
N(2)-C(9)	1.327(4)	1.316(5)	1.317(4)			
C(11)-C(12)-N(1)	106.2(2)	106.3(3)	122.8(3)			
C(11)-N(1)-C(6)	128.38(2	129.4(2)	129.5(3)			
N(1)-C(5)-C(6)	119.4(2)	119.3(3)	118.4(3)			
Cp-pyrazole twist angle	71.90	34.45	43.08			
N(2)-N(1)-C(4)-C(5), \phi1	-47.0	-34.35	49.0			
C(10)-N(1)-C(6)-C(5), \phi2	-43.6	-51.4	45.0			
The interatomic distances are reported in angstroms (Å); angles are (°)						

 Table S2. Structural parameters for N-arylated ferrocenyl pyrazoles 2-4

 Table S3. The electrochemical data for N-arylated ferrocenyl pyrazoles 1-4

Entry	Epa	Epc	ipc/ipa	E1/2	ΔΕ
	(mV)	(mV)	(mV)	(mV)	(mV)
Ferrocene	532	453	0.91	492	79
H (1)	708	645	1.0	694.5	67
CF3 (2)	742	668	1.0	705	74
CN (3)	730	652	1.1	691	78
NO ₂ (4)	710	634	1.1	672	76

Entry	Experi	imental da	ata		Calculated (TD-DFT) data (gas phase)			
	$\lambda (nm)^a$	^{<i>b</i>} <i>Е</i> номо	^b Elumo	$^{c}E_{g}^{optical}$	$^{d}E_{\rm HOMO}$	^d ELUMO	Oscillator	^d B.G
		(eV)	(eV)	(eV)	(eV)	(eV)	Strength, f	(eV)
H (1)	360	-5.165	-1.721	3.444	-5.669	-1.239	0.0260	3.9300
CF3 (2)	379	-5.191	-1.92	3.271	-5.706	-1.711	0.0121	3.5283
CN (3)	374	-5.174	-1.859	3.315	-5.716	-2.122	0.0309	3.9348
NO ₂ (4)	384	-5.149	-1.85	3.229	-5.732	-3.236	0.0166	3.1007

Table S4. Comparison of experimental (CV/UV-Vis) and the calculated (DFT) HOMO-LUMO values for N-arylated ferrocenyl pyrazoles 1-4

^aCalculated as λ^{onset} values are from absorption graphs in CH₃CN solvent

^bCalculated as HOMO and LUMO level obtained from CV using Eqs

^bE^{optical} onset values obtained from oxidation peak in a cyclic voltammogram.

$$E_{HOMO} = -e[E_{ox}^{onset} + 4.4]$$

 $E_{LUMO} = E_{g}^{optical} + E_{HOMO}$

^cCalculated as optical band gap calculated from absorption onset/edge using the equation $e[E_g^{optical}] = 1240/\lambda_{onset}$.

^d Theoretically calculated HOMO, LUMO and band gap values from DFT calculations

Table S5. Solvatochromic data [\tilde{v} max (Cm⁻¹) of the charge transfer band] for N–arylated ferrocenyl pyrazoles **1-4** in different solvents with π^* values by Kamlet and Taft

C - l 4 -		0	-*				Δῦmax
Solvents	α	р	n. –	H (1)	CF ₃ (2)	CN (3)	NO ₂ (4)
THF	0	0.55	0.58	35.33	35.08	36.96	34.84
DCM	0.13	0.1	0.82	35.08	34.96	35.21	34.96
CHCl ₃	0.2	0.1	0.58	36.23	37.17	37.03	36.76
EtOAc	0	0.45	0.54	45.05	36.36	36.36	36.49
MeOH	1	0.66	0.69	45.24	36.49	36.49	36.1
EtOH	0.83	0.75	0.62	43.1	42.19	41.32	41.49
ACN	0.35	0.4	0.75	36.36	41.32	42.19	45.05
DMF	0	0.71	0.88	43.29	44.84	45.45	42.37
DMSO	0	0.76	1	47.16	48.78	47.39	49.5

Entry	Excitation	τ1	τ2	τ3	α1	A 2	QL 3	χ^2
	(nm)							
H (1)	375	3.215	8.651	4.916	2.247	0.057	0.010	1.299
CF ₃ (2)	375	3.716	9.394	4.623	2.049	0.069	0.011	1.096
CN (3)	375	1.729	7.581	3.724	1.847	0.024	0.005	1.086
NO ₂ (4)	375	5.627	9.858	3.160	2.095	0.122	0.051	1.403

 Table S6. Fluorescence lifetime details for N-arylated ferrocenyl pyrazoles 1-4

Table S7. Selected transitions obtained from B3LYP/6-31+G** level theory for N-arylatedferrocenyl pyrazoles 1-4

Entry	λ(nm)	D.M (Debye)	Oscillator strength, <i>f</i>	Energy (eV)	Major Contribution
H (1)	315.48	7.82	0.0260	3.9300	$H \rightarrow L$ (51.04%) H-1 →L (19.93%) $H \rightarrow L+2$ (8.5%)
CF3 (2)	351.40	6.72	0.0121	3.5283	H→L (67.45%) H→L+2 (10.04%)
CN (3)	315.10	7.41	0.0309	3.9348	H-2 →L (86.46%) H-3 →L (7.39%)
$NO_{2}(4)$	399.86	7.81	0.0166	3.1007	H-3→L (96.86%)

Table S8. Density surfaces of the frontier orbitals involved in the electronic transitions of the N–arylated ferrocenyl pyrazoles 1-4 derived from TD-DFT at iso surface value of 0.02 a.u

Orbitals	H (1)	CF ₃ (2)	CN (3)	$NO_2(4)$
НОМО-3				
HOMO-2				
HOMO-1				
номо				
LUMO				
LUMO+1				
LUMO+2				

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