Electronic Supplementary Information

Pendant chain engineering to fine-tune nanomorphology and solid state luminescence in naphthalimide AIEEgens: application to phenolic nitro-explosive detection in water

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1. Materials, Apparatus and methods

All starting materials, reagents and analytes (4-bromo-1,8-naphthalene anhydride, 8hydroxyquinolene, α -naphthol, alkylamines, nitroaromatics, deuterated solvents) were purchased from Sigma Aldrich (INDIA). HPLC grade solvents and potassium carbonate were purchased from Zenith India and Northeast Chemicals. The chemicals purchased were of reagent grade and used without additional purification.

(*Caution!* Nitroaromatic analytes, especially TNP, are categorized as secondary chemical explosives and should be handled carefully with safety measures)

NMR (¹H, ¹³C) spectra were recorded with a Bruker Avance 600 MHz NMR spectrometer by taking residual solvent signal as internal reference. Electro spray ionization mass (ESI-MS) spectra were recorded on a Waters (Micro mass MS-Technologies) Q-Tof MS Analyzer spectrometer. Perkin-Elmer Model Lambda-35 spectrophotometer and Horiba Fluoromax-4 spectrofluorometer have been used to record UV/vis and PL spectra respectively in a 3 ml quartz cuvettes of path length 1 cm at 298 K. Fluorescence quantum yields in solutions were calculated by standard methods using Quinine sulphate ($\Phi_F = 0.577$ in 0.1 M H₂SO₄, $\lambda_{ex} = 350$ nm). Solid state absorbance and emission were recorded with Fluoromax-4 fluorescence spectrophotometer equipped with a Quanta-\u00f6 integrating sphere to get solid state fluorescence quantum yield. Hydrodynamic diameters of the nanoaggregates were obtained in a Malvern Zetasizer instrument. Life-time measurements were performed using a MicroTime-200 instrument. FE-SEM images were obtained on Sigma Carl ZEISS field emission scanning electron microscope by drop casting the aqueous solution on aluminium foil and were left for drying at room temperature. The ground state optimized geometries were obtained using B3LYP hybrid functional incorporated in the Gaussian 09 package.^{1,2} The 6-31G(d) basis set for all the atoms has been used in all calculations, which offers reasonably high quality outcomes at a reasonable time.

2. Synthesis

Alkylation: To a suspension of 4-bromonaphthalene anhydride (554.2 mg, 2 mmol) in ethanol, butylamine (146.28 mg, 2 mmol) was added drop wise at room temperature. The temperature was increased and stirred for 8 hours at 85 °C. The mixture was cooled and the solvent was evaporated under reduced pressure. The solid residue was dissolved in chloroform and washed with water for two times. The organic layer was concentrated after drying over anhydrous Na₂SO₄. Finally column purification was performed to obtain the pure product (**BN**).

Similar procedures were followed by taking equal equivalents of respective alkyl or cycloalkylamines to get the other Alkylated 4-bromonaphthalimides derivatives (HN, ON, CHN and MCHN) as mentioned in Scheme 1.

BN: Light grey solid (595 mg, 89% yield); M.p. 100-102 °C; HRMS (*m/z*): calcd for C₁₆H₁₄BrNO₂ 331.0208; found 332.0280 [M+H]⁺; ¹H NMR (600 MHz, CDCl₃, δ ppm) 8.44 (d, 1H), 8.34 (d, 1H), 8.20 (d, 1H), 7.82 (d, 1H), 7.63 (t, 1H), 3.97 (t, 2H) 1.52 (m, 2H), 1.26 (m, 2H), 0. 78 (t, 3H); ¹³C NMR (150.00 MHz, CDCl₃, δ ppm) 163.79, 133.35, 132.16, 131.36, 131.25, 130.77, 130.34, 129.14, 128.24, 123.32, 122.46, 40.57, 30.35, 20.56, 14.02.

HN: Light green solid (615 mg, 85% yield); M.p. 92-93 °C; HRMS (*m/z*): calcd for C₁₈H₁₈BrNO₂ 359.0521; found 360.0600 [M+H]⁺; ¹H NMR (600 MHz, CDCl₃, δ ppm) 8.57 (d, 1H), 8.46 (d, 1H), 8.32 (d, 1H), 7.94 (d, 1H), 7.77 (t, 1H), 4.12 (t, 3H) 1.70 (m, 2H), 1.31 (m, 6H), 0.87 (t, 3H); ¹³C NMR (150.00 MHz, CDCl₃, δ ppm) 163.63, 163.60, 133.22, 132.06, 131.25, 131.16, 130.61, 130.24, 128.98, 128.15, 123.21, 122.34, 40.78, 31.71, 28.18, 26.96, 22.74, 14.25.

ON: Light brown solid (620 mg, 80% yield); M.p. 85-86 °C; HRMS (*m/z*): calcd for C₂₀H₂₂BrNO₂ 387.083; found 388.0950 [M+H]⁺; ¹H NMR (600 MHz, CDCl₃, δ ppm) 8.64 (d, 1H), 8.54 (d, 1H), 8.39 (d, 1H), 8.02 (d, 1H), 7.83 (t, 1H), 4.15 (t, 2H) 1.71 (m, 2H), 1.34 (m, 10H), 0.87 (t, 3H); ¹³C NMR (150.00 MHz, CDCl₃, δ ppm) 163.73, 133.32, 132.15, 131.34, 131.24, 130.74, 130.32, 129.11, 128.22, 123.31, 122.45, 40.82, 32.00, 29.51, 29.40, 28.27, 27.32, 22.83, 14.28.

CHN: White solid (586 mg, 82% yield); M.p. 82-83 °C; HRMS (m/z): calcd for C₁₈H₁₆BrNO₂ 357.063; found 358.0455 [M+H]⁺; ¹H NMR (600 MHz, CDCl₃, δ ppm) 8.62 (d, 1H), 8.52 (d, 1H), 8.37 (d, 1H), 8.01 (d, 1H), 7.83 (t, 1H), 4.15 (m, 1H) 2.54 (m, 2H) 1.90 (m, 2H), 1.74 (m, 2H), 1.45 (m, 2H), 0.87 (m, 2H); ¹³C NMR (150.00 MHz, CDCl₃, δ ppm) 164.02, 163.98, 132.82,

131.88, 131.85, 131.10, 131.06, 130.40, 129.67, 128.96, 123.64, 122.78, 54.11, 29.71, 29.08, 26.49, 25.42, 22.83.

MCHN: White solid (645 mg, 86% yield); M.p. 72-74 °C; HRMS (m/z): calcd for C₁₈H₁₆BrNO₂ 371.053; found 372.0633 [M+H]⁺; ¹H NMR (600 MHz, CDCl₃, δ ppm) 8.63 (d, 1H), 8.53 (d, 1H), 8.38 (d, 1H), 8.01 (d, 1H), 7.82 (t, 1H), 4.04 (d, 2H) 1.88 (m, 1H) 1.67 (m, 5H), 1.17 (m, 5H); ¹³C NMR (150.00 MHz, CDCl₃, δ ppm) 164.12, 133.35, 132.28, 131.48, 131.26, 130.79, 130.34, 129.21, 128.26, 123.29, 122.43, 46.34, 36.88, 32.11, 31.14, 29.89, 26.53, 26.06.

Post functionalization: To different round bottom flasks, each containing the solution of **BN**, **HN**, **ON**, **CHN** and **MCHN** (0.5 mmol) in dry DMF (5 mL), 1 mmol of 8-hydroxyquinoline (for HNN, α -naphthol was taken) and 200 mg of K₂CO₃ were added to them separately and were refluxed for 15 hours. The solvents were vaporized under vacuum and the residues were extracted with chloroform (30×3 mL). The organic layers were washed with H₂O for several times followed by washing with brine and dried over anhydrous Na₂SO₄. The crude products were concentrated and purified through column chromatography over silica gel to get the final products (**BNQ**, **HNQ**, **ONQ**, **CHNQ**, **MCHNQ** and **HNN**) respectively.

BNQ: Light yellow solid (164 mg, 82 % yield); M.p. 177-179 °C; HRMS (*m/z*): calcd for C₂₅H₂₀N₂O₃ 396.147; found 397.1581 [M+H]⁺; ¹H NMR (600 MHz, CDCl₃, δ ppm) 8.87 (m, 2H), 8.67 (d, 1H), 8.39 (d, 1H), 8.27 (d, 1H), 7.79 (m, 2H), 07.58 (d, 1H), 7.49 (d, 1H), 7.46 (d, 1H), 6.75 (d, 1H), 4.18 (t, 2H), 1.72 (m, 2H), 1.45 (m, 2H), 0.98 (t, 3H), ¹³C NMR (150.00 MHz, CDCl₃, δ ppm) 164.71, 164.06, 160.58, 151.30, 150.99, 141.41, 136.48, 132.90, 132.05, 129.24, 129.18, 129.05, 126.95, 126.71, 126.65, 125.64, 124.06, 122.36, 120.28, 116.84, 111.57 40.53, 30.45, 20.60, 14.05.

HNQ: Yellow solid (155 mg, 73 % yield); M.p. 168-170 °C; HRMS (*m/z*): calcd for C₂₇H₂₄N₂O₃ 424.1787; found 425.1894 [M+H]⁺; ¹H NMR (600 MHz, CDCl₃, δ ppm) 8.85 (d, 2H), 8.64 (d, 1H), 8.37 (d, 1H), 8.24 (d, 1H), 7.76-7.79 (m, 2H), 07.57 (t, 1H), 7.46 (d, 2H), 6.72(d, 1H), 4.14 (t, 2H), 1.70 (m, 2H), 1.32 (m, 6H), 86 (t, 3H), ¹³C NMR (150.00 MHz, CDCl₃, δ ppm) 164.58, 163.93, 160.51, 151.11, 150.91, 141.31, 136.42, 132.84, 131.95, 130.24, 129.81, 129.16, 126.89, 126.62, 125.63, 123.91, 122.72, 122.29, 120.32, 116.84, 111.39, 40.53, 31.72, 28.25, 26.97, 22.73, 14.25.

ONQ: White solid (182 mg, 80 % yield); M.p. 150-153 °C; HRMS (*m/z*): calcd for C₂₉H₂₈N₂O₃ 452.210; found 453.2165 [M+H]₊; ₁H NMR (600 MHz, CDCl₃, δ ppm) 8.86 (d, 2H), 8.66 (d, 1H), 8.39 (d, 1H), 8.26 (d, 1H), 7. 79 (d, 2H), 07.59 (t, 1H), 7.48 (m, 2H), 6.74(d, 1H), 4.16 (t, 2H), 1.72 (m, 2H), 1.25-1.43 (m, 10H), 0.87 (t, 3H), ₁₃C NMR (150.00 MHz, CDCl₃, δ ppm) 164.69, 164.04, 160.56, 151.30, 150.98, 141.41, 136.51, 132.89, 132.04, 130.35, 129.94, 129.22, 126.96, 126.69, 125.65, 123.89, 122.76, 122.37, 120.30, 116.94, 111.35, 40.62, 32.02, 29.55, 29.43, 28.37, 27.37, 22.83, 14.28.

CHNQ: Light pink solid (170 mg, 80.5 % yield); M.p. 167-169 °C; HRMS (*m/z*): calcd for $C_{27}H_{22}N_2O_3$ 422.163; found 423.1719 [M+H]⁺; ¹H NMR (600 MHz, CDCl₃, δ ppm) 8.87 (d, 1H), 8.84 (d, 1H), 8.64 (d, 1H), 8.37 (d, 1H), 8.26 (d, 1H), 7.78 (m, 2H), 7.58 (t, 1H), 7.44 (d, 1H), 7.43 (d, 1H), 6.75(d, 1H), 5.02 (m, 1H), 2.55 (m, 2H), 1.87 (m, 2H), 1.72 (m, 3H), 0.88 (m, 3H), ¹³C NMR (150.00 MHz, CDCl₃, δ ppm) 165.11, 164.49, 160.24, 151.45, 150.95, 141.38, 136.47, 132.76, 131.92, 130.33, 129.91, 128.91, 126.93, 126.71, 125.50, 123.94, 122.73, 122.53, 120.08, 116.92, 111.79, 53.84, 29.89, 29.34, 26.78, 25.69, 22.88.

MCHNQ: Yellow solid (162 mg, 74 % yield); M.p. 189-191 °C; HRMS (*m/z*): calcd for $C_{28}H_{24}N_2O_3$ 436.178; found 437.1878 [M+H]⁺; ¹H NMR (600 MHz, CDCl₃, δ ppm) 8.87 (m, 2H), 8.66 (d, 1H), 8.39 (d, 1H), 8.27 (d, 1H), 7.80 (m, 2H), 7.59 (d, 1H), 7.46 (d, 1H), 7.45 (d, 1H), 6.75(d, 1H), 4.05 (d, 2H), 1.72 (m, 1H), 1.63 (m, 2H), 1.22 (m, 4H), 0.88 (m, 3H), ¹³C NMR (150.00 MHz, CDCl₃, δ ppm) 165.03, 164.39, 160.54, 151.30, 150.98, 141.39, 136.51, 133.00, 132.15, 130.34, 129.97, 129.22, 126.96, 126.70, 125.64, 123.99, 122.70, 122.37, 120.28, 116.95, 111.58, 46.23, 36.96, 32.12, 31.19, 29.89, 26.59, 26.11.

HNN: Light grey solid (189 mg, 89 % yield); M.p. 112-114 °C; HRMS (*m/z*): calcd for C₂₈H₂₅NO₃ 423.183; found 424.1926 [M+H]⁺; ¹H NMR (600 MHz, CDCl₃, δ ppm) 8.88 (dd, 1H), 8.70 (dd, 1H), 8.38 (d, 1H), 7.93 (m, 2H), 7.83 (m, 2H), 7.54 (m, 2H), 7.28 (t, 1H), 6.77(d, 1H), 4.16 (t, 2H), 1.72 (m, 2H), 1.62 (m, 2H), 1.32 (m, 5H), 0.88 (t, 3H), ¹³C NMR (150.00 MHz, CDCl₃, δ ppm) 164.41, 163.73, 160.19, 150.36, 135.21, 132.91, 131.91, 129.71, 128.47, 128.24, 126.99, 126.75, 126.73, 126.63, 125.91, 125.90, 123.54, 122.74, 121.44, 116.90, 116.61, 110.31, 40.42, 31.58, 28.09, 26.82, 22.59, 14.10.

3. Preparation of stock solutions for aggregation and sensing studies

Stock solutions of all the naphthalimides were prepared in DMF at a concentration of 1×10^{-2} M. Stock solutions of nitroaromatic compounds like trinitrophenol (TNP), 2,4-dinitrophenol (2,4-DNP), 2,6-dinitrophenol (2,6-DNP), 4-nitrophenol (p-NP), 2-nitrophenol (o-NP) and phenol were prepared in Milli-Q water at a concentrations of 1×10^{-2} M. Nitroaromatics, namely, trinitrotoluene (TNT), 2,4-dinitrotoluene (2,4-DNT), 2,4-dinitrobenzene (1,3-DNB), 2-nitrotoluene (o-NT), 3-nitrotoluene (m-NT), 4-nitrotoluene (p-NT), nitrobenzene (NB), nitromethane (NM), 2,3-dimethyl-2,3-dinitrobutane (DMNB), 2,6-dinitrotoluene (2,6-DNT), 1,4-dinitrobenzene (1,4-DNB) were prepared at concentrations of 1×10^{-2} M in 1:1 methanol:water solvent system. The stock solution of each naphthalimide was diluted to 20 μ M in water and HEPES buffer (pH 7) for each titration in a 3 mL quartz cuvette (1 cm × 1 cm). The stock solutions of nitroaromatics were introduced in portions and the fluorescence intensity changes were recorded at room temperature ($\lambda_{ex} = 360$ nm).

4. Quantum Yield Calculations

PL quantum yields (Φ_s) of naphthalimides were calculated by taking quinine sulfate ($\Phi_s = 0.57$ in 0.1 M H₂SO₄) as standard and using the equation shown below:

$$\Phi_{\rm s} = \Phi_{\rm r} \left(A_r F_s / A_s F_r \right) \left(\eta_s^2 / \eta_r^2 \right)$$

Where, s and r represent sample and reference, Φ signifies the quantum yield, A denotes absorbance, F signifies relative integrated fluorescence intensity, and η represents the refractive index of the medium.

5. Cyclic Voltammetry Studies

Electrochemical measurements were performed in a three-electrode cell with platinum wire as counter electrode, glassy carbon as working electrode and saturated $Ag/AgNO_3$ electrode as reference electrode. The Fc⁺/Fc couple was employed as internal reference and Tetrabutylammoniumhexafluorophosphate (0.1 M) in acetonitrile was taken as supporting electrolyte. All the measurements were carried out at room temperature under inert atmosphere. Single reduction peak was observed for HNQ. The LUMO level (- 3.0234 eV) was calculated from

the onset method $[E_{LUMO} = -(E_{(onset, red vs Fc+/Fc)} + 4.8) (eV)]$. Band gap (3.1234 eV) of HNQ was determined from the onset of UV–visible spectrum to calculate its HOMO level (- 6.1468 eV).



6. Computational study

Figure S1. Optimized structures in electronic ground state with electron density of HOMO and LUMO (Gaussian 09, DFT B3LYP 6-31G basis set). Energy of HOMO, LUMO and band gaps are in eV, dipole moments are in debye and dihedral angels are in "o" with respect to naphthalimide and quinoline/naphthalene plane. (Left to Right: **BNQ, HNQ, ONQ, CHNQ, MCHNQ** and **HNN**).

7. Aggregation study

Table S1. Photophysical properties of Naphthalimide AIEgens with various f_w in DMF at 20 μ M concentration.

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	DMF	[nm]	[M ⁻¹ cm ⁻¹]	[nm]	Δλ/nm	[%] ^c	(solid)
	0%	363	2882.525	435	72	3.57	
	20%	365	3103.35	438	73	2.53	
RNO	40%	365	2913.575	442	77	1.60	16.9±1.2
D'''X	60%	369	2247.975	443	74	1.23	
	80%	371	2028.475	444	73	0.89	
	99.8%	374	2466.625	474	100	10.77	
	0%	362	3125.425	435	73	3.76	
	20%	365	2971.475	439	74	3.15	
HNO	40%	368	2816.45	457	89	2.11	
····· \ X	60%	391	2755	493	102	1.31	9.4±0.0
	80%	389	2530.775	494	105	8.78	
	99.8%	390	2879.6	494	104	13.06	
	0%	363	3100	438	75	12.17	21.3±0.8
	20%	365	3204.575	441	76	9.05	
ONO	40%	366	2325.25	445	79	7.30	
Unix	60%	368	2206.45	447	79	28.98	
	80%	369	2959.25	448	79	22.37	
	99.8%	370	3074.1	457	87	19.51	
CHNQ	0%	363	2808.95	436	73	4.10	26.1±1.1
	20%	365	3233.3	443	78	3.25	
	40%	366	2485.075	443	77	2.41	
	60%	367	2216.225	447	80	1.52	
	80%	368	2206.675	438	70	1.73	
	99.8%	389	2959.9	464	75	17.70	
MCHNQ	0%	363	2721.125	438	75	4.05	
	20%	365	2652.25	444	79	3.50	
	40%	366	2310.225	444	78	2.13	27.0±0.9
	60%	368	2474.075	442	74	1.32	
	80%	365	1940.35	444	79	1.27	

	99.8%	373	2601.45	457	84	29.79	
HNN	0%	362	3400.925	412	50	1.64	
	20%	364	3457.475	411	47	1.01	11.7±0.8
	40%	366	3404.375	429	63	1.16	
	60%	368	3069.7	429	61	2.36	
	80%	370	3601.175	482	112	15.42	
	99.8%	383	3915.85	481	98	12.16	

^aMeasured at each absorption maximum. ^bExcited at 360 nm for all compounds. ^cQuantum yields were calculated by using quinine sulfate (0.1 M H₂SO₄, λ_{ex} =350 nm, Φ_{FL} = 57.7%) solution as reference together with the following formula: $\Phi_{FL}=\Phi_{FL}(I/I_R)(A_R/A)(\eta^2/\eta_R^2)$, where Φ = quantum yield, I = Intensity of emission, A = absorbance at λ_{ex} , η = refractive index of solvent, R = reference. (20 μ M)

Absorption and emission spectra at different water fraction in DMF (at 25 °C, 20 μ M, λ_{ex} = 360 nm)



Figure S2. Absorption (left) and emission spectra (right) of BNQ.



Figure S3. Absorption (left) and emission spectra (right) of HNQ.



Figure S4. Absorption (left) and emission spectra (right) of ONQ.



Figure S5. Absorption (left) and emission spectra (right) of CHNQ.



Figure S6. Absorption (left) and emission spectra (right) of MCHNQ.



Figure S7. Absorption (left) and emission spectra (right) of HNN.



Figure S8. Emission spectra in 99.8% water-0.2% DMF. (20 μ M, λ_{ex} 360 nm)



8. DLS Studies of Aggregates (99.8% Water-0.2% DMF mixture solution at 25 °C, 20 μ M)





Figure S10. Size distribution by DLS of ONQ aggregate [Left] and CHNQ aggregate [Right].



Figure S11. Size distribution by DLS of MCHNQ aggregate [Left] and HNN aggregate [Right].

9. Sensing studies



Figure S12. [Left] Effect of increasing concentration of 2,4-DNP on the fluorescence spectra of **HNQ** (20 μ M at pH 7) at room temperature. [**Right**] Stern–Volmer plots for the fluorescence quenching of **HNQ** by 2,4-DNP.



Figure S13. [Left] Effect of increasing concentration of p-NP on the fluorescence spectra of HNQ (20 μ M at pH 7) at room temperature. [Right] Stern–Volmer plots for the fluorescence quenching of HNQ by p-NP.



Figure S14. Extent of fluorescence quenching of the naphthalimides nanoaggregates observed upon the addition of 70 μ M TNP in aqueous media.

10. Detection limit calculations



Figure S15. Change in fluorescence emission intensity of HNQ at different concentrations of TNP.

 $LOD = 3 \times S.D. / k$

LOD for TNP = $3 \times 1015.514 / 4.12 \times 10^{10}$

$$= 73.79 \times 10^{-9} \,\mathrm{M}$$
 (16.8 ppb)

Using the above formula (LOD = $3 \times$ S.D. / k), LOD for TNP was also calculated in other N-atom containing congeners.



Figure S16. Change in fluorescence emission intensity of **BNQ** at lower concentrations of TNP. LOD = 123.32 nM (28.2 ppb)



Figure S17. Change in fluorescence emission intensity of CHNQ at lower concentrations of TNP. LOD = 86.03 nM (19.7 ppb)



Figure S18. Change in fluorescence emission intensity of **MCHNQ** at lower concentrations of TNP. LOD = 78.08 nM (17.9 ppb)



Figure S19. Change in fluorescence emission intensity of **ONQ** at lower concentrations of TNP. LOD = 113.74 nM (26.0 ppb)

11.¹H-NMR, ¹³C-NMR, Mass and IR Spectra











¹H spectra of HN



¹³C spectra of HN



[S19]

Mass spectra of HN







Mass spectra of ON



¹H spectra of CHN







Mass spectra of CHN







¹H spectra of BNQ



¹³C spectra of BNQ



Mass spectra oh **BNQ**



¹H spectra of HNQ

[S26]



¹³C spectra of HNQ



Mass spectra of HNQ



IR Spectra of HNQ



¹H spectra of ONQ



¹³C spectra of ONQ



Mass spectra of ONQ



¹H spectra of CHNQ



¹³C spectra of CHNQ



Mass spectra of CHNQ





¹H spectra of MCHNQ



¹³C spectra of MCHNQ



Mass spectra of MCHNQ



¹H spectra of HNN



230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

¹³C spectra of HNN



Mass spectra of HNN



IR Spectra of MCHNQ

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