Supplementary Information

Orange Red Emitting Naphthalene Diimide Derivative Containing Dendritic Wedges: Aggregation Induced Emission (AIE) and Detection of Picric acid (PA) in Aqueous Medium

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Synthesis of compound A

[Chemical reaction diagram]

Scheme. S1 Synthetic scheme for compound A.

Methyl-4-dihydroxybenzoate (2 g, 0.014 mole), potassium carbonate (3.86 g, 0.027 mole) and 40 mL 1,4-dioxane were taken in a 250 mL round bottom flask. 1-chloro methyl naphthalene (3.7 g, 0.02 mole) was added followed by the addition of a catalytic amount of tertiary butyl ammonium iodide (0.48 g, 0.0013 mole). The solution mixture was refluxed for 24 hours. Solvent was evaporated and extracted with ethyl acetate water mixture. The organic layer was dried over anhydrous Na$_2$SO$_4$. The solid was then crystallized from methanol to get compound A (3.9 g, 91 %); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 3.9 (s, 3H), 5.55 (s, 2H), 7.06 (t, 2H), 7.44-7.6 (m, 4H), 7.82 (m, 2H), 8.02 (d, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 52.07, 68.9, 114.7, 123.16, 125.4, 126.21, 126.80, 126.78, 126.88, 128.97, 129.46, 131.85, 133.99, 162.74, 167.01. IR(KBr) $\nu$ = 1925, 1874, 1787, 1701, 1650, 1629, 1535, 1513, 1477, 1383, and 1318 cm$^{-1}$.

Synthesis of compound A-1

[Chemical reaction diagram]

Scheme. S2 Synthetic scheme for compound A-1.

Compound A (2.5 g, 0.008 mole) and hydrazine monohydrate (19.40 mL, 0.4 mole) were dissolved in MeOH (30 mL) and THF (15 mL). The reaction mixture was stirred at 60°C for 12 hours. After the reaction mixture was cooled to room
temperature, solvent was evaporated by applying vacuum. The residue was dissolved in DCM and washed many times with water to remove excess of hydrazine mono hydrate. The organic layer was then dried over anhydrous Na$_2$SO$_4$. Crude product was purified by column chromatography ethyl acetate /Hexane (3:7)mixture as eluent. (2.2 g, 88%); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.37 (s,2H), 5.49(s,2H),7.03(s,2H),7.43-7.59(m,4H),7.73(d,2H), 7.87(m,2H), 7.89(d,1H). $^{13}$C NMR (100 MHz,CDCl$_3$): $\delta$ 68.80, 114.91, 123.51, 125.31, 126.04, 126.61, 126.70, 128.77, 129.29, 131.43, 131.58, 133.81, 161.73, 168.30. IR(KBr) $\nu$ =3209, 3050, 2920, 2476,1790, 1761, 1718, 1682, 1610, 1581, 1538,1509,1451,1386 and 1314 cm$^{-1}$. ESI-MS : m/z Calcd for C$_{28}$H$_{26}$N$_{2}$O$_{2}$:292.33, found: 293[M+H]$^+$. 

Synthesis of compound B

Scheme.S2 Synthetic scheme for compound B.

Methyl-3, 5-dihydroxybenzoate (2 g, 0.0118 mole), potassium carbonate (4.8 g, 0.035 mole) and 40 mL of 1,4-dioxane were taken in 250 mL round bottom flask. 1-chloro methyl naphthalene (5.25 g, 0.0297 mole) was added followed by the addition of a catalytic amount of tertiary butyl ammonium iodide (0.5 g, 0.0013 mole). The solution mixture was refluxed for 24 hours. Solvent was evaporated and extracted with ethyl acetate water mixture. The organic layer was dried over anhydrous Na$_2$SO$_4$. The solid was crystallized from methanol to get B (4.8, 86 %); $^1$H NMR (500 MHz,CDCl$_3$): $\delta$ 3.86 (s, 3H), 5.43 (s, 4H), 7.87 (d, 1H), 7.37-7.54 (m, 10H),7.82 (m,4H),7.97(s,2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 52.34,69.04,107.43,108.63,123.71,125.35,126.02,126.59,126.80,128.77,129.29,131.59,131.88,132.29,133.85,160.0,166.85.1 R(KBr) $\nu$ = 3138, 2490, 1719, 1513, 1433, 1367, 1315, 1263, 1155 and 1042 cm$^{-1}$. ESI-MS: m/z Calcd for C$_{30}$H$_{24}$O$_4$:448.51, found: 471[M+Na]$^+$. 

Synthesis of compound B-1

Scheme.S3 Synthetic scheme for compound B-1.

Compound B (2 g, 0.0044 mole) and hydrazine monohydrate (10.8 mL, 0.22 mole) were dissolved in MeOH (30 mL) and THF (15 mL). The reaction mixture was stirred at 60˚C for 12 hours. After the reaction mixture was cooled to room temperature, solvent was evaporated by applying vacuum. The residue was dissolved in DCM and washed many times with
water to remove excess of hydrazine mono hydrate. The organic layer was then dried over anhydrous Na$_2$SO$_4$. Crude product was purified by column chromatography ethyl acetate /Hexane (3:7) mixture as eluent. (1.8 g, 90%); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 4.04 (s,2H), 5.34(s,4H), 6.85(t,1H), 7.08(d,2H), 7.49-7.53(m,6H), 7.57(s,2H), 7.81-7.87 (m,2H), 7.96 (d,2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 69.02, 105.7, 106.19, 123.62, 125.32 ,126.0, 126.6, 126.7, 128.7, 129.2, 131.51, 133.82, 134.9, 137.1, 160.26, 168.42. IR(KBr) $\nu$ = 3345, 3131, 2490, 1825, 1767, 1686, 1628, 1554, 1458, 1379 and 1281 cm$^{-1}$. ESI-MS : m/z Calcd for C$_{29}$H$_{24}$N$_2$O$_3$:448.51, found: 471[M+Na]$^+$. 

**Synthesis of compound C**

Scheme. S4 Synthetic scheme for compound C.

Methyl-3,4, 5-dihydroxybenzoate (3 g, 0.016 mole) ,potassium carbonate (13.5g, 0.097mole) and 100 mL of 1,4-dioxane were taken in 250 mL round bottom flask . 1-chloro methyl naphthalene (9.89 g, 0.055 mole) was added followed by the addition of a catalytic amount of tertiary butyl ammonium iodide (0.59 g, 0.0016 mole). The solution mixture was refluxed for 24 hours. Solvent was evaporated and extracted with ethyl acetate water mixture. The organic layer was dried over anhydrous Na$_2$SO$_4$. The solid was crystallized from methanol to get C ( 8.4 g, 86 %); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 4.12 (s,3H), 5.5(s,2H), 5.7(s,4H) 6.7(t,1H), 7.38(t,2H), 7.59-7.68(m,7H), 7.76-7.84(m,7H), 8.02(m,5H), 8.29(d,2H).$^{13}$CNMR (100MHz, CDCl$_3$): $\delta$ 52.33, 69.90, 73.28, 109.07, 123.84, 124.38, 124.91, 125.37, 125.44, 125.62, 125.76, 125.96, 126.12, 126.59, 127.05, 127.32, 127.9, 128.69, 128.75, 129.19, 131.83, 132.03, 132.86, 133.41, 133.81, 142.59, 153.07, 166.74. IR(KBr) $\nu$ =3131, 3042, 2969, 2482, 1885, 1768, 1694, 1627, 1576, 1526, 1475, 1418, 1324, and 1224 cm$^{-1}$. ESI-MS : m/z Calcd for C$_41$H$_{32}$O$_5$: 604.69, found: 627[M+Na]$^+$. 

**Synthesis of compound C-1**

Scheme. S5 Synthetic scheme for compound C-1.

Compound C (2 g, 0.0033 mole) and hydrazine monohydrate (8.0 mL, 0.165 mole) were dissolved in MeOH (30 mL) and THF (15 mL). The reaction mixture was stirred at 60°C for 12 hours. After the reaction mixture was cooled to room
temperature, solvent was evaporated by applying vacuum. The residue was dissolved in DCM and washed many times with water to remove excess of hydrazine mono hydrate. The organic layer was then dried over anhydrous Na$_2$SO$_4$. Crude product was purified by column chromatography 30 % ethyl acetate/Hexane (3:7) mixture as eluent. (1.8g, 90%). $^1$H NMR (500 MHz, CDCl$_3$): δ 3.1(S,2H), 5.3 (s,2H), 5.52 (s,4H), 7.07(t,2H), 7.2(s,1H), 7.26(s,2H), 7.3-7.53 (m,9H), 7.65(m,3H) 7.8-7.8 (m,5H), 8.05(d,2H). $^{13}$C NMR (100MHz,CDCl$_3$): δ 70.03, 73.35, 106.85, 123.7, 124.3, 124.9, 125.35, 125.48, 125.9, 126.62, 126.9, 127.39, 127.94, 128.71, 128.83, 129.19, 131.55, 137.85, 131.89, 132.79, 133.42, 133.78, 141.71, 153.35. IR(KBr) ν =3323, 3116, 2497, 1812, 1752, 1693, 1621, 1534, 1464 and 1381 cm$^{-1}$. ESI-MS: m/z Calcd for C$_{40}$H$_{32}$N$_2$O$_4$: 604.69, found: 627[M+Na]$^+$. 

**Synthesis of compound I**

Naphthalene dianhydride (1 g, 0.0037 mole) and A-1(2.48, 0.0085) were taken in 30 mL of dry DMF and was heated to 140°C for 12 hours. The reaction mixture was allowed to cool down to room temperature. The reaction mixture was extracted with DCM and washed many times with water. Organic layer was then dried over anhydrous Na$_2$SO$_4$. Solvent The crude product was then purified by column chromatography methanol /CHCl$_3$(1:9) mixture as eluent to obtain a brown coloured powder (2.5g, 82% yield). $^1$H NMR (500 MHz, DMSO-d$_6$): δ 5.71(s,4H), 7.35(d,4H), 7.5-7.65 (m,6H), 7.4(d,2H), 7.9-8.1 (m,14H), 8.8(s,4H), 11.4 (d,2H). $^{13}$C NMR (100MHz, DMSO-d$_6$): δ 68.0, 114.86, 123.81, 123.36, 126.01, 126.5, 126.77, 128.49, 128.81, 129.86, 131.05, 131.53, 131.61, 131.97, 133.26, 160.84, 161.83, 164.66. IR(KBr) ν =3586, 3277, 3052, 1728, 11690, 1658, 1601, 1508, 1540, 1500, 1419, 1381, 1355, 1280, 1243, 1202, 1173, 1124, 1098 cm$^{-1}$. MS (MALDI-TOF): m/z Calcd for C$_{50}$H$_{32}$N$_4$O$_8$: 816.81, found: 839.26[M+Na]$^+$. 

**Synthesis of compound II**

Naphthalene dianhydride (1 g, 0.0037 mole) and B-1(3.8g, 0.0085) were taken in 30 mL of dry DMF and was heated to 140°C for 12 hours. The reaction mixture was allowed to cool down to room temperature. The reaction mixture was extracted with DCM and washed many times with water. Organic layer was then dried over anhydrous Na$_2$SO$_4$. The crude product was then purified by column chromatography methanol/CHCl$_3$(1:9) to obtain a yellowish brown powder (3.4 g, 81% yield). $^1$H NMR (500 MHz, DMSO-d$_6$): δ 5.6(s,8H), 7.1(s,1H), 7.3(s,4H) 7.4-7.56 (m,12H), 7.66(m,5H), 7.8-7.9(m,10H), 8.07(m,5H), 8.6(d,4H), 11.5(d,2H). $^{13}$C NMR (100 MHz, DMSO-d$_6$): δ 68.77, 70.5, 107.51, 124.2, 125.8, 126.53, 127.0,
128.79, 129.63, 131.8, 132.47, 133.98, 141.68, 160.2, 161.2. IR(KBr) ν = 3374, 3131, 2999, 1899, 1862, 1767, 1694, 1629, 1548, 1505, 1446, 1369 and 1265 cm⁻¹. MS (MALDI-TOF): m/z Calcd for C₇₂H₄₈N₃O₁₁: 1129.17, found: 1151.54[M +Na]⁺.

Synthesis of compound III

Scheme S8 Synthetic scheme for compound III.

Naphthalene dianhydride (1.5 g, 0.0056 mole) and C-1 (7.77 g, 0.0128 mole) were taken in 30 mL of dry DMF and was heated to 140 °C for 12 hours. The reaction mixture was extracted with DCM and washed many times with water. Organic layer was then dried over anhydrous Na₂SO₄. The crude product was then purified by column chromatography methanol/CHCl₃ (1:9) to obtain a dark brown powder (6.5 g, 80% yield).

¹H NMR (500 MHz, DMSO-d₆): δ 5.2 (s, 4H), 5.74 (s, 8H), 6.39 (t, 2H), 6.96 (t, 2H), 7.08 (t, 2H), 7.25 (t, 2H), 7.54 (s, 14H), 7.75 - 7.8 (t, 2H), 8 (s, 9H), 8.23 (s, 5H), 8.84 (s, 4H), 11.63 (d, 2H).

¹³C NMR (100 MHz, DMSO-d₆): δ 72.41, 107.01, 124.0, 124.2, 124.7, 125.41, 126.0, 126.56, 127.18, 127.82, 128.48, 128.66, 128.9, 131.2, 131.29, 132.19, 132.5, 132.87, 133.39, 140.38, 152.7, 160.99, 164.58. IR(KBr) ν = 3359, 3142, 2991, 2478, 1908, 1872, 1764, 1684, 1619, 1525, 1446, 1410, and 1316 cm⁻¹. MS (MALDI-TOF): m/z Calcd for C₉₄H₆₄N₃O₁₃: 1441.53, found: 1464.268[M +Na]⁺.
Fig. S1 UV-Vis and emission spectra of compound II (a,b) and III (c,d) in THF at different concentrations; black-10^-4 M, red-0.5 x 10^-4 M, green-10^-5 M, sky blue -0.5x 10^-5 M and navy blue-10^-6 M, (Inset of a shows enlarged UV spectra from 400nm-700 nm).

Table S1: Quantum yield measurement of compound I-III in different solvents with quinine sulphate 10^-5 M in 0.05 N H_2SO_4 as standard (\(\phi_R = 0.6 \pm 2\)) (Error % ;\(\pm 5\))
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<th>$\lambda_{\text{max}}$ (nm)</th>
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Fig. S3 UV-Vis and emission spectra of compound I (a, b) and compound III (c, d) in THF(10^-5 M) with different water fraction λw; 350 nm.

Fig. S4 Lifetime plot for compound I (a), compound II (b) and compound III (c) in THF(10^-5 M) with different water fraction λw; 340 nm.

Fig. S5 UV-VIS spectra of compound I (a) II (b) and III (c)[10^-3 M] in solution and film state.
Fig. S6 Excitation spectra of compounds I-III in the film state emission collected at 590 nm.

Fig. S7 TGA thermogram of compound I-III.
Fig. S8 SXRD, WXRD pattern of compound II (a,b) and compound III (c,d).

Fig S9 VT-FTIR spectra of compound I (a) and compound III (b).

Fig. S10 variable temperature NMR spectra of compound I [1.7x10^{-2} M] (a) and compound II [3.5 x10^{-2} M] (b) in DMSO-d6 from 30°C to 120°C. Variable temperature NMR spectra of compound II [5.3 x10^{-3} M] in CDCl3 from -40°C to 50°C.
Table S2: Lifetime values for compounds I-II for the addition of different fraction of water.

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Fig. S11 SEM images of compound I (above) and compound III (below) with different fraction of water: a) 30% water, b) 50%, and c) 90% water.
Fig. S12 (Above) TEM images of compound I (a), compound II (b), and compound III (c) with 90% water fraction (scale 0.1 μm). (Below) DLS spectra of compound a) I b) II and c) III with 90% water fraction (10⁻⁵ M).

Fig. S13 Quenching percentage and selectivity for different analytes (a). Fluorescence intensity at 590 nm for the addition of different equivalent of PA(b).

Fig. S14 (Left) Detection of PA in film for compound II. (Right) photographs showing quenching in luminescence by the addition of 10 μm [10⁻³ M] PA on TLC stripes under UV illumination.
Fig. S15(Above) Lifetime plot for compound II before and after addition of PA. (Below) SEM images of compound II THF/Water(1:9) (a), after the addition of PA (b).
Fig. S 16 $^1$H-NMR spectra of I DMSO-$d_6$.

Fig. S 17 $^{13}$CNR spectra of I DMSO-$d_6$. 
Fig. S18 $^1$H-NMR spectra of II DMSO-$d_6$.

Fig. S19 $^{13}$C-NMR spectra of II DMSO-$d_6$. 
Fig. S20 $^1$H- NMR spectra of III DMSO-$d_6$.

Fig. S21 $^{13}$C -NMR spectra of III DMSO-$d_6$. 
Fig. S22 MALDI-TOF of compound I.

Fig. S23 MALDI-TOF of compound II.
Fig. S24 MALDI-TOF of compound III.