Supporting Information for

Tunable and switchable control of luminescence through multiple physical stimulations in aggregation-based monocomponent systems

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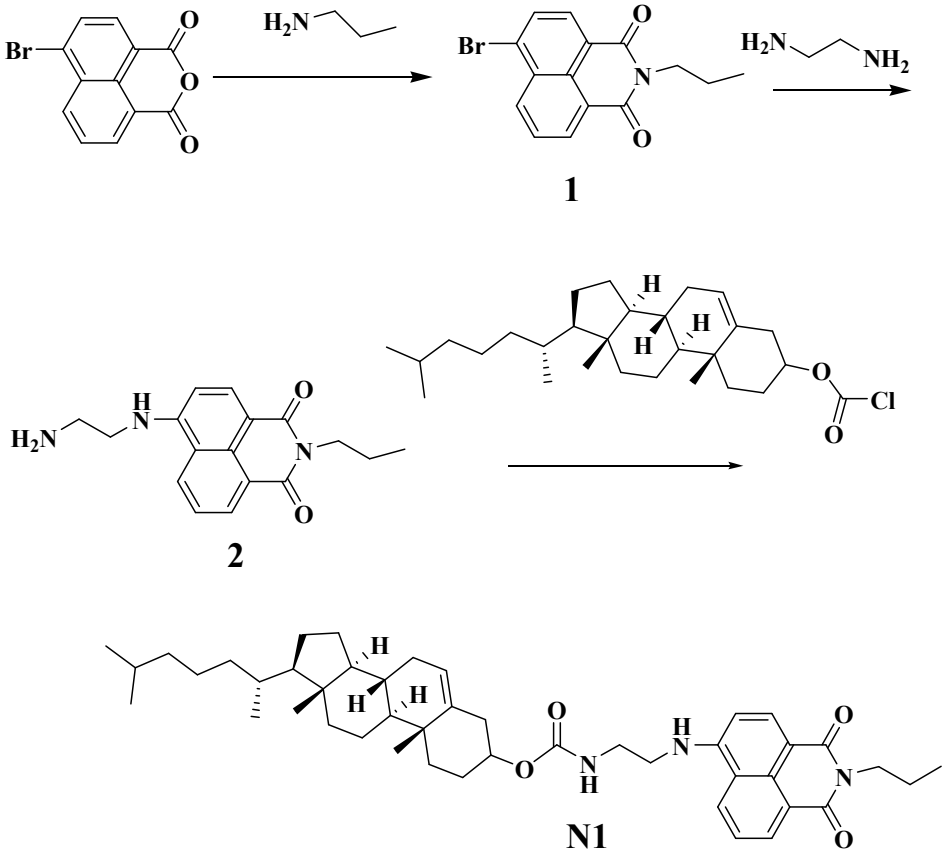
Content

1. Synthesis details of the compounds

1.1 Synthesis of N1



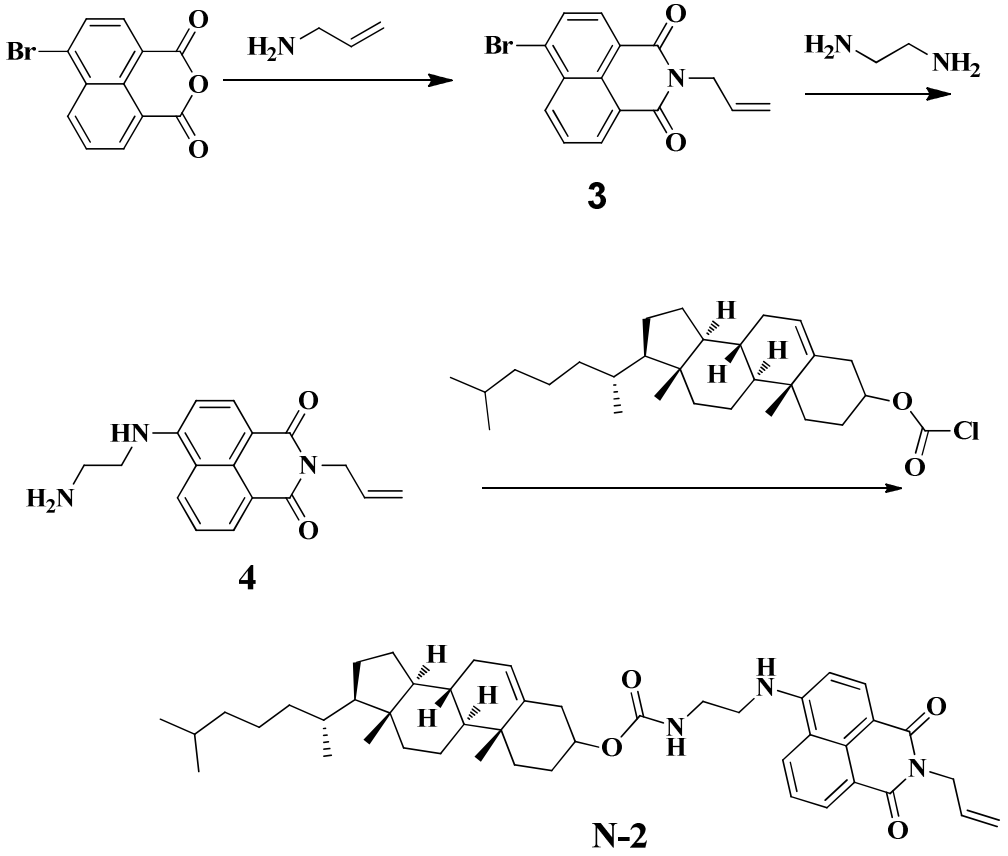
Scheme S1 Synthesis procedure of **N1**

Synthesis of compound 1: 1 was synthesized according to literature 1. 4-Br-1, 8-naphthalic anhydride (277 mg, 1 mmol), and propylamine (59 mg, 1 mmol) was refluxed in ethanol for 8 hours. The mixture was then concentrated and purified by column chromatography (SiO_2: CH_2Cl_2/CH_3OH = 100: 1) to yield **1** as a white solid (191 mg, 60%). Mp. 135-137 °C; ^{1}HNMR (400M, $CDCl_3$, δ ppm): 1.00-1.03 (t, J = 7.6 Hz, 3H), 1.74-1.80 (m, 2H), 4.12-4.16 (t, J =7.6 Hz, 2H), 7.83-7.87 (t, J = 8 Hz, 1H), 8.03-8.05 (d, J = 8 Hz, 1H), 8.40-8.42 (d, J = 8.8 Hz, 1H), 8.55-8.58 (d, J = 8.4 Hz, 1H), 8.66-8.67 (d, J = 7.2 Hz, 1H); HRMS calcd for $C_{15}H_{12}BrNO_2Na$ $[M+Na]^+$, 339.9949, 341.9922; Found: 339.9941, 341.9922.

Synthesis of compound 2: 1 (318 mg, 1 mmol) and ethylenediamine (600 mg, 10 eq) were refluxed in ethanol for 72 hours. The mixture was then concentrated, and washed with water. The filtrate was then purified by column chromatography (SiO_2: CH_2Cl_2/CH_3OH = 10: 1) to yield **2** as a yellow solid (127 mg, 40%). Mp. 56-58 °C. ^{1}HNMR (500M, $CDCl_3$, δ ppm): 1.00-1.03 (t, 3H, J = 2.5 Hz), 1.75-1.80 (m, 2H), 3.18-3.20 (m, 2H), 3.42-3.45 (m, 2H), 4.12-4.15(t, 2H, J = 7.5 Hz), 6.70-6.71 (d, 1H, J = 8 Hz), 7.60-7.63 (t, 1H, J = 8 Hz), 8.18-8.20 (d, 1H, J = 8.5 Hz), 8.45-8.47 (d, 1H, J = 8.5 Hz), 8.57-8.59 (d, 1H, J = 8.5 Hz); HRMS calcd for $C_{17}H_{20}N_3O_2$ $[M+H]^+$, 299.1589; found, 299.1590.

Synthesis of N1: 2 (297 mg, 1mmol), cholesterol-5-ene-3-beta-chloroformate (449 mg, 1mmol) and 1 mL Et_3N were stirred for 24 hours, then the mixture was concentrated and purified by column chromatography (SiO_2: CH_2Cl_2/CH_3OH = 50: 1) to yield **N1** as a yellow solid (426 mg, 60%). Mp. 171-173 °C; ^{1}H NMR (500 M, $CDCl_3$, δ, ppm): 0.672 (s, 3H), 0.86 (d, 3H, J = 2 Hz), 0.87-0.88 (d, 3H, J = 2 Hz), 0.91-2.36 (m, 41 H), 3.47-3.48 (m, 2H), 3.67-3.69 (t, 2H, J = 6 Hz), 4.55-4.62 (m, 1H), 5.36 (m, 1H), 8.57-8.59 (d, 1H, J = 8 Hz), 7.62-7.65 (d, 1H, J = 8 Hz), 8.22-8.23 (d, 1H, J = 8.5 Hz), 8.43-8.45 (d, 1H, J = 8.5 Hz), 8.57-8.58 (d, 1H, J = 8.5 Hz); ^{13}CNMR (125 M, $CDCl_3$, δ, ppm): 11.64, 11.92, 18.78, 9.33, 21.10, 21.54, 22.63, 22.89, 23.90, 24.34, 28.08, 28.13, 28.29, 31.90, 31.97, 35.85, 36.25, 36.62, 36.96, 38.54, 39.58, 39.78, 39.91, 41.72, 42.37, 46.59, 50.07, 56.20, 56.76, 75.54, 103.43, 110.13, 120.44, 122.87, 122.96, 124.85, 126.96, 129.84, 131.16, 134.54, 139.59, 150.01, 158.77, 164.32, 164.85; HRMS calcd for $C_{45}H_{64}N_3O_4$ $[M+H]^+$: 711.4930; found: 711.4925.

1.2 Synthesis of N2



Scheme S2 Synthesis procedure of **N2**

3 and **4** were synthesized according to literature 2.

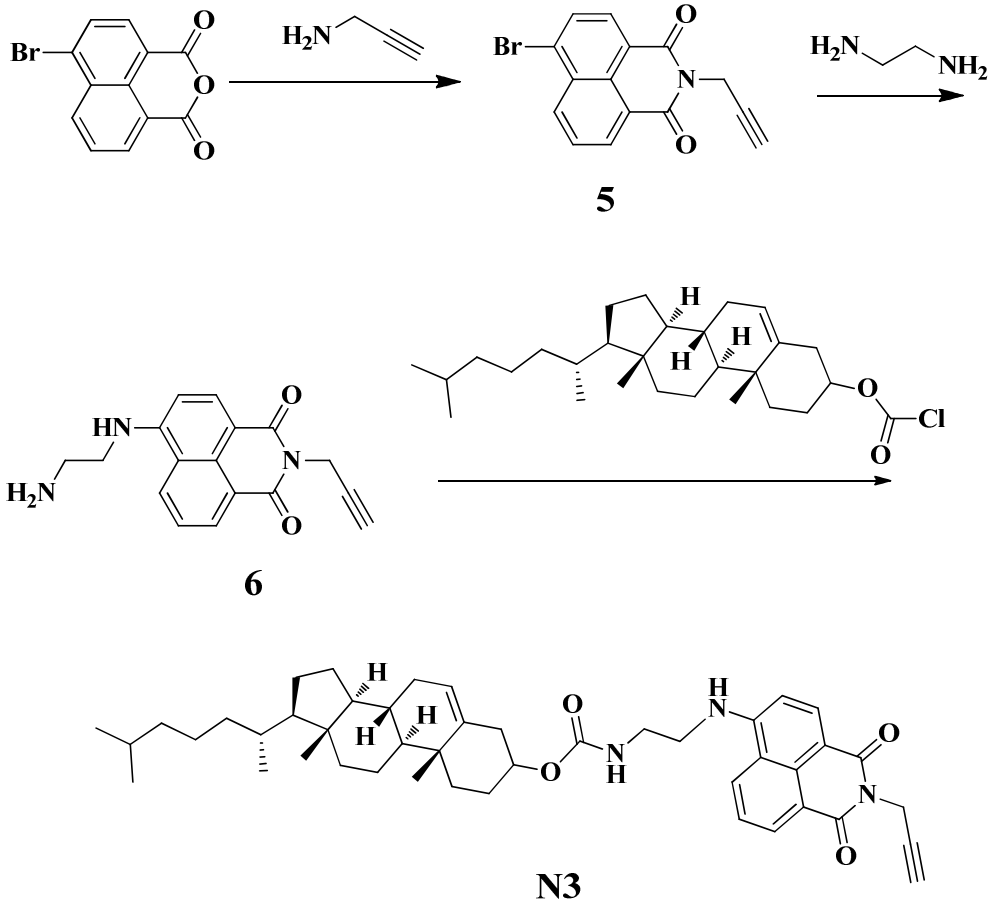
Synthesis of 3: 4-Br-1, 8-naphthalic anhydride (277 mg, 1 mmol), and allylamine (57 mg, 1 mmol) was refluxed in ethanol for 8 hours. The mixture was then concentrated and purified by column chromatography (SiO_2: CH_2Cl_2/CH_3OH = 100: 1) to yield **3** as a white solid (354 mg, 50%). Mp. 154-156 °C. ^1H NMR (500 M, $CDCl_3$, δ, ppm): 4.80-4.81 (d, 2H, J = 5.5 Hz), 5.21-5.23 (d, 1H, J = 10 Hz), 5.31-5.35 (d, 1H, J = 10 Hz), 7.84-7.87 (t, 1H, J = 8 Hz), 8.04-8.06 (d, 1H, J = 8 Hz), 8.42-8.43 (d, 1H, J = 8 Hz), 8.57-8.59 (d, 1H, J = 8.5 Hz), 8.66-8.68 (d, 1H, J = 8.5 Hz).

Synthesis of 4: 3 (314 mg, 1 mmol)**,** ethylenediamine (600 mg, 10 eq) were refluxed in ethanol for 8 hours, then ethanol was removed under vacuum, and the reaction mixture was crystallized by ethanol and water (with the volume ration of 1: 1) to

yield **4** as a yellow solid (103 mg, 35%). Mp. 139-143 °C; ^{1}H NMR (500 M, $CDCl_3$, δ, ppm): 3.21-3.24 (t, 2H, J = 6 Hz), 3.45-3.48 (m, 2H), 4.15-4.19 (t, 2H, J = 7.5 Hz), 5.34 (s. 1H), 6.74-6.76 (d, 1H, J = 7.5 Hz), 7.65-7.68 (t, 1H, J = 7.5 Hz), 8.22-8.24 (t, 1H, J = 8.5 Hz), 8.49-8.51 (d, 1H, J = 8.5 Hz), 8.62-8.64 (d, 1H, J = 8.5 Hz); HRMS calcd for $(C_{17}H_{17}N_3O_2)^+$ $[M+H]^+$: 295.1321; found: 295.0678.

Synthesis of N2: 4 (295 mg, 1 mmol), cholesterol-5-ene-3-beta-chloroformate (449 mg, 1 mmol) and 1 mL Et_3N were stirred for 24 hours, then the mixture was concentrated and purified by column chromatography (SiO_2: CH_2Cl_2/CH_3OH = 50: 1) to yield **1** as a yellow solid (411 mg, 58%). Mp: 133-135 °C; ^{1}H NMR (500 M, $CDCl_3$, δ, ppm): 0.66 (s, 3H), 0.85 (d, 3H, J = 2.5 Hz), 0.86-0.87 (d, 3H, J = 2.5 Hz), 0.90-2.36 (m, 35H), 3.46-3.48 (t, 3H, J = 4 Hz), 3.64-3.70 (m, 3H), 4.10-4.13 (t, 2H, J = 7.5 Hz), 4.54-4.61 (m, 1H), 5.35 (s, 1H), 6.57-6.58 (d, 1H, J = 8.5 Hz), 7.61-7.64 (t, 1H, J = 8.5 Hz), 8.21-8.23 (d, 1H, J = 8.5 Hz), 8.43-8.44 (d, 1H, J = 8.5 Hz), 8.56-8.58 (d, 1H, J = 8.5 Hz); ^{13}C NMR (125 M, $CDCl_3$, δ): 11.82, 12.10, 19.03, 19.41, 21.05, 21.49, 22.85, 23.09, 23.72, 24.31, 31.87, 35.64, 36.16, 36.54, 37.03, 38.39. 38.69, 41.23, 42.34, 43.37, 49.96, 55.32, 56.11, 56.57, 73.67, 104.20, 108.47, 120.71, 122.46, 124.73, 128.85, 129.93, 131.07, 134.53, 151.12, 163.40, 164.23; HRMS calcd for $C_{45}H_{62}N_3O_4$ $[M+H]^+$: 710.4807; found: 710.4898.

1.3 Synthesis of N3



Scheme S3 Synthesis procedure of **N3**

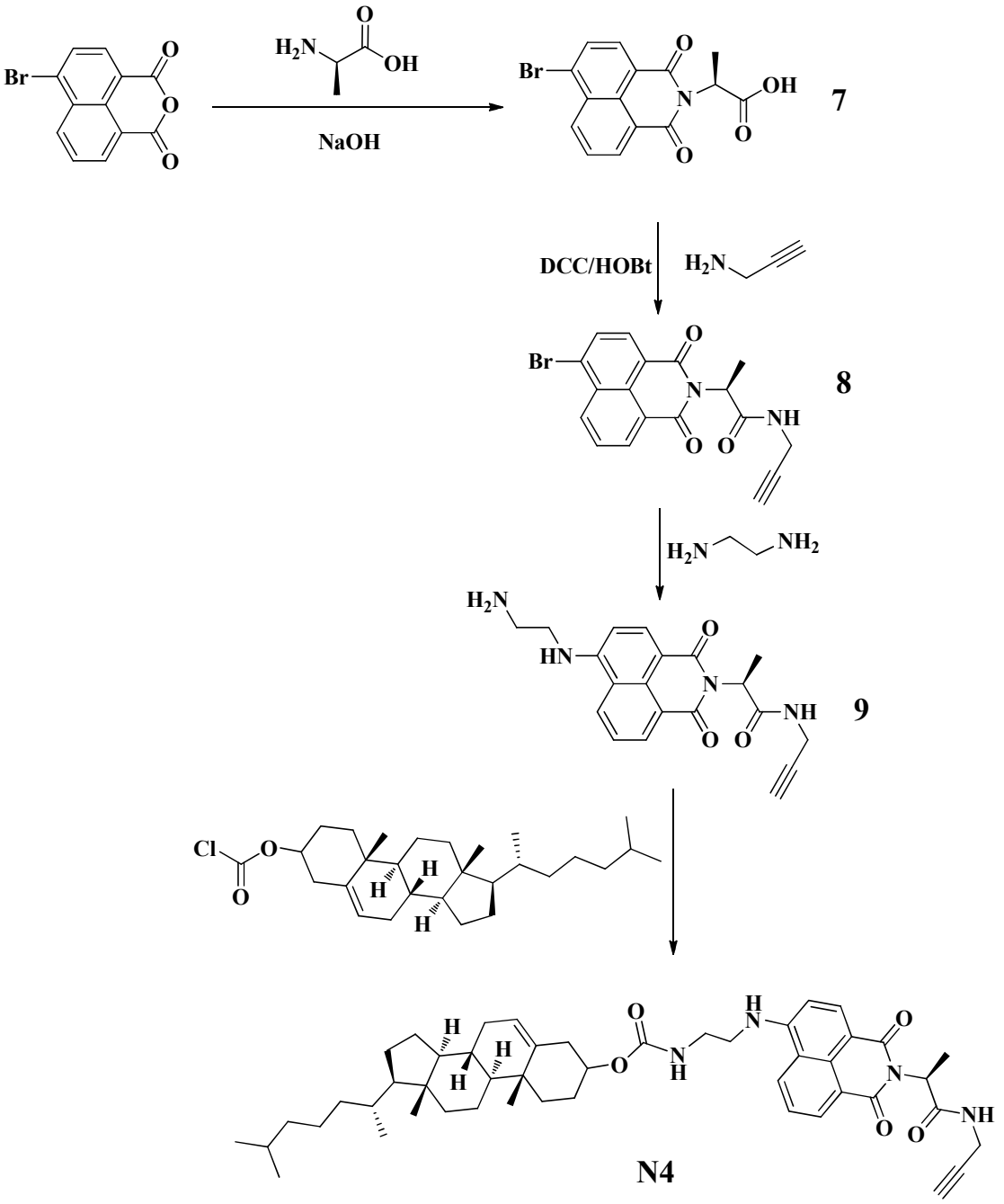
Synthesis of 5: 4-Br-1, 8-naphthalic anhydride (277 mg, 1 mmol), and propargylamine (54 mg, 1 mmol) was refluxed in ethanol for 8 hours. The mixture was then concentrated and purified by column chromatography (SiO_2: CH_2Cl_2/CH_3OH = 100: 1) to yield **5** as a white solid (191 mg, 60%). Mp: 239-241 °C; ^{1}HNMR (500 M, $CDCl_3$, δ, ppm): 2.22-2.23 (t, 1H, J = 2.5 Hz), 4.98 (d, 2H, J = 2.5 Hz), 7.88-7.91 (t, 1H, J = 8 Hz), 8.08-8.10 (d, 1H, J = 8 Hz), 8.48-8.50 (d, 1H, J = 7.5 Hz), 8.64-8.63 (d, J = 8.5 Hz), 8.72-8.74 (d, 1H, J = 7.5 Hz); ^{13}C NMR (125 M, $CDCl_3$, δ): 29.56, 70.72, 78.33, 121.89, 122.77, 128.17, 130.73, 130.79, 131.21, 131.60, 132.46, 133.72, 162.81; HRMS calcd for $(C_{15}H_9BrNO_2)^+$ $[M+H]^+$: 313.9817, 315.9790; found: 313.9807, 315.9790.

Synthesis of 6: 5 (313 mg, 1 mmol)**,** ethylenediamine (600 mg, 10 eq) were refluxed

in ethanol for 8 hours, then ethanol was removed under vacuum, and the reaction mixture was purified by column chromatography to yield **6** as a yellow solid (118 mg, 40%). Mp: 217-219 °C; ^{1}HNMR (400M, $CDCl_3$, δ, ppm): 2.16-2.17 (t, 1H, J = 2.4 Hz), 3.18-3.20 (t, J = 6 Hz, 2H), 3.40-3.45 (t, J = 6 Hz, 2H), 4.95-4.96 (d, J = 2. 4 Hz, 2H), 6.71-6.73 (d, J = 8.8 Hz, 1H), 7.62-7.66 (t, J = 7.6 Hz, 1H), 8.19-8.21 (d, J = 8.4 Hz, 1H), 8.49-8.51 (d, J = 8.4 Hz, 1H), 8.62-8.64 (d, J = 7.2 Hz, 1H); ^{13}CNMR (125 M, $CDCl_3$, δ, ppm): 29.11, 47.02, 72.93, 84.44, 104.46, 107.45, 120.59, 121.86, 124.70, 129.52, 129.93, 131.38, 135.00, 151.69, 162.47, 163.52; HRMS calcd for $(C_{17}H_{15}N_3O_2+H)^+$ $[M+H]^+$: 294.1243; found: 294.1242.

Synthesis of N3: 6 (294 mg, 1 mmol), cholesterol-5-ene-3-beta-chloroformate (449 mg, 1 mmol) and 1 mL Et_3N were stirred for 24 hours, then the mixture was concentrated and purified by column chromatography (SiO_2: CH_2Cl_2/CH_3OH = 50: 1) to yield **N3** as a yellow solid (353 mg, 50%). Mp: 205-207 °C; ^{1}H NMR (400 M, $CDCl_3$, δ, ppm): 0.67 (s, 3H), 0.86 (d, J = 2 Hz, 3H), 0.87 (d, J = 2 Hz, 3H), 0.97-2.26 (m, 35 H), 3.50-3.51 (t, J = 6 Hz, 2H), 3.78-3.80 (t, J = 6 Hz, 2H), 4.55-4.62 (m, 1H), 4.96 (d, 2H, J = 2 Hz), 5.32-5.33 (m, 1H), 6.58-6.59 (d, 1H, J = 6.8 Hz), 7.66-7.70 (t, J = 6Hz, 1H), 6.28-6.30 (d, J = 6.8 Hz, 1H), 8.47-8.49 (d, J = 6.8 Hz, 1H), 8.62-8.63 (d, J = 5.6 Hz, 1H); ^{13}C NMR (125 M, $CDCl_3$, δ): 11.87, 18.73, 19.29, 21.06, 22.57, 22.83, 23.84, 24.29, 28.03, 28.08, 28.23, 29.16, 31.86, 31.94, 35.80, 36.20, 36.58, 36.91, 38.49, 39.53, 39.74, 42.34, 46.67, 50.04, 56.16, 56.72, 69.98, 79.31, 103.48, 109.55, 120.46, 122.53, 122.86, 124.88, 129.94, 131.53, 135.00, 137.51, 139.53,150.36, 158.81, 163.31, 164.06; HRMS calcd for $(C_{45}H_{60}N_3O_4)^+$ $[M+H]^+$: 706.4584; found: 706.4564.

1.4 Synthesis of N4



Scheme S4 Synthesis procedure of **N4**

The synthesis of **7** could be seen in literature 3.

Synthesis of 8 : Compound **7** (348 mg, 1 mmol), propargylamine (54 mg, 1 mmol), DCC (206 mg, 1 mmol), and HOBt (135 mg, 1 mmol) were stirred in $CHCl_3$ for 24

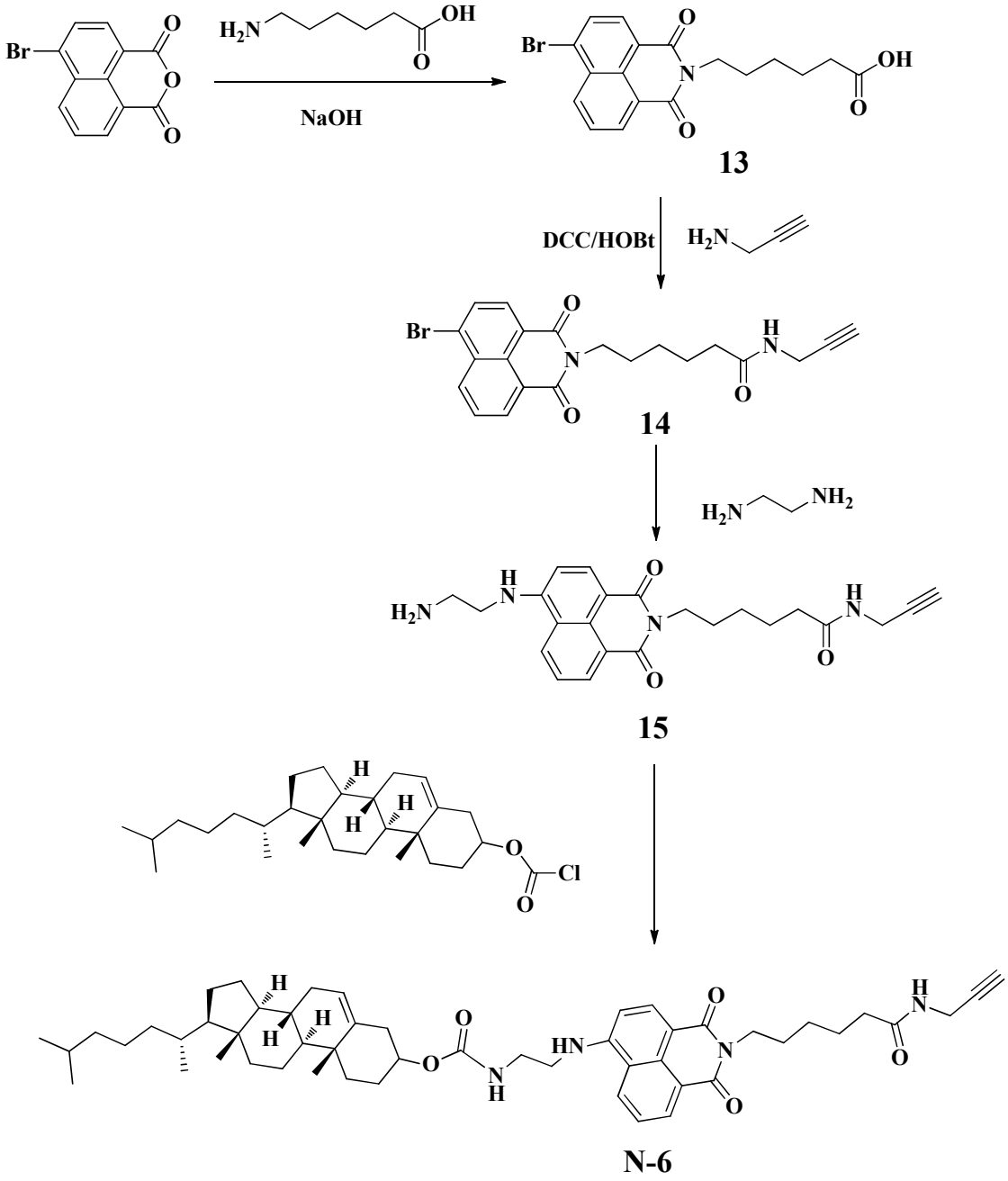
hours, then the reaction mixture was concentrated and purified by column chromatography (SiO_2: CH_2Cl_2/CH_3OH = 50: 1) to yield **8** as a white solid (231 mg, 60%). Mp. 259-260 °C ; ^{1}H NMR (400M, $CDCl_3$, δ): 1.72-1.74 (d, 3H, *J* = 7.2 Hz), 2.24-2.25 (t, *J* = 2.4 Hz, 1H), 4.13-4.14 (t, *J* = 2.4 Hz, 2H), 5.70-5.75 (m, 1H), 7.84-7.88 (t, *J* = 8 Hz, 1H), 8.04-8.06 (d, *J* = 8 Hz, 1H), 8.40-8.42 (d, *J* = 8 Hz, 1H), 8.58-8.60 (d, *J* = 8.4 Hz, 1H), 8.65-8.66 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (125 M, DMSO-d_6): 29.11, 47.02, 72.93, 80.44, 104.46, 107.45, 120.59, 121.88, 124.70, 129.52, 129.92, 131.38, 135.00; HRMS calc. for $[C_{18}H_{13}BrN_2O_3+Na]^+$: 407.0007, 408.9987; Found: 408.9987, 407.0005.

Synthesis of 9: Compound **8** (1 mmol, 385 mg/mL)**,** ethylenediamine (600 mg, 10 eq) were refluxed in ethanol for 48 hours, the reaction mixture was then concentrated and washed with water, the filtrate was purified by column chromatography (SiO_2: CH_2Cl_2/CH_3OH = 20: 1) to yield **9** as yellow solid (109 mg, 30%). Mp. 202-204 °C; ^{1}H NMR (500 M, $CDCl_3$, δ): 1.69-1.71 (d, 3H, *J* = 7.0 Hz), 2.28 (s, 1H), 3.12-3.14 (t, *J* = 6 Hz, 2H), 3.35-3.38 (m, 2H), 4.20-4.21 (t, *J* = 2 Hz, 2H), 5.74-5.78 (m, 1H), 6.49-6.50 (d, 1H, *J* = 7.5 Hz), 7.35-7.38 (t, *J* = 7.5 Hz, 1H), 8.16-8.18 (d, *J* = 8 Hz, 1H), 8.21-8.23 (d, *J* = 8.5 Hz, 1H), 8.25-8.26 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (125 M, DMSO-d_6): 14.91, 28.72, 46.81, 49.32, 73.03, 81.94, 104.25, 108.56, 120.59, 122.89, 124.64, 129.00, 130.20, 131.09, 134.71, 151.28, 163.11, 164.04, 169. 91; HRMS calc. for $[C_{20}H_{20}N_4O_3+H]^+$: 365.1614; Found: 365.1600.

Synthesis of N4: Compound **9** (364 mg, 1 mmol), cholesterol-5-ene-3-beta-y chloroformate (449 mg, 1 mmol) and 1 mL Et_3N were stirred for 24 hours, then the mixture was concentrated and purified by column chromatography (SiO_2: CH_2Cl_2/CH_3OH = 50: 1) to yield **N4** as a yellow solid (357 mg, 46%). Mp. 277-279 °C; ^{1}HNMR (400M, $CDCl_3$, *δ*): 0.67 (s, 3H), 0.86 (d, 3H, *J* = 2 Hz), 0.87-0.88 (d, 3H, *J* = 2 Hz), 0.91-2.38 (m, 39 H), 3.45-3.46 (t, 2H, *J* = 4.5 Hz), 3.64-3.67 (t, 2H, *J* = 4.5 Hz), 4.15-4.16 (t, 2H, *J* = 2 Hz), 4.56-4.63 (m, 1H), 5.76-5.80 (m, 1H), 6.49-6.51 (d, 1H, *J* = 8.5 Hz), 7.50-7.52 (t, 1H, *J* = 8.5 Hz), 8.23-8.24 (d, 1H, *J* = 8.5 Hz), 8.31-8.33 (d, 1H, *J* = 8.5 Hz), 8.40-8.41 (d, 1H, *J* = 7 Hz). ^{13}C NMR (125 M, DMSO-d_6): 12.14, 14.89, 19.03, 19.46, 21.04, 22.88, 23.15,

23.70, 24.33, 27.88, 28.27, 28.72, 31.80, 31.84, 35.68, 36.14, 36.52, 37.02, 38.72, 42.32, 43.25, 49.32, 49.92, 56.06, 56.57, 73.03, 73.64, 81.92, 104.08, 108.86, 120.63, 122.34, 122.97, 124.75, 128.81, 130.20, 131.10, 134.61, 140.15, 151.04, 156.58, 163.08, 164.01, 169.84; HRMS calc. for $[C_{48}H_{64}N_4O_5]^+$: 777.4955; Found: 777.4949.

1.5 Synthesis of N5



Scheme S5 Synthesis procedure of **N5**

Synthesis of compound 10: A mixture of aminocaproic acid (1 mmol, 131 mg), and sodium hydroxide (40 mg, 1 mmol) was stirred at 40 ℃ for 20 minutes, then 4-Br-1,8-naphthalic anhydride (277 mg, 1 mmol) was added, and refluxed for 24 hours under nitrogen atmosphere. The reaction mixture was concentrated in vacuum, the residue was neutralized by dilute hydrochloric acid, and purified by column chromatography (SiO_2: CH_2Cl_2/CH_3OH = 20: 1) to yield **10** as a white solid (179 mg, 46%). Mp: 166-168 °C. ^{1}HNMR (400M, $CDCl_3$, δ): 1.45-1.52 (m, 2H, CH_2), 1.69-1.80 (m, 4H, CH_2), 2.36-2.40 (t, 2H, J = 7.6 Hz, CH_2), 4.16-4.19 (t, 2H, J = 7.6 Hz, CH_2), 4.43-4.60 (m, 1H), 7.83-7.87 (t, 2H, J = 7.2 Hz, ArH), 8.03-8.05 (d, 1H, J = 8 Hz, ArH), 8.40-8.42 (d, 1H, J = 8 Hz, ArH), 8.56-8.58 (d, 1H, J = 7.2 Hz), 8.64-8.67 (d, 1H, J = 7.2 Hz, ArH). ^{13}CNMR (125M, $CDCl_3$, δ): 24.68, 26.51, 27.60, 33.96, 122.11, 122.89, 128.39, 129.01, 129.48, 129.97, 131.19, 131.61, 131.83, 132.81. HRMS calc. for $[C_{18}H_{16}BrNO_4+H]^+$: 390.0296, 392.0276; Found: 390.0328, 392.0310.

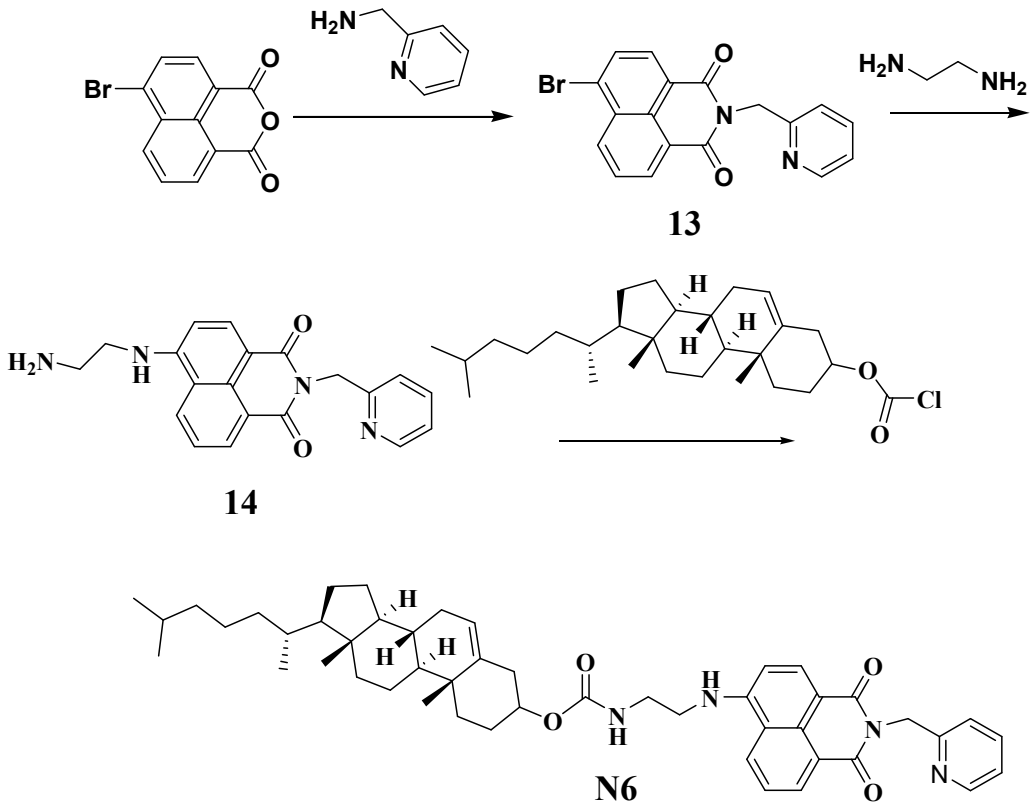
Synthesis of compound 11: Compound **10** (390 mg, 1 mmol), propargylamine (54 mg, 1 mmol), DCC (618 mg, 3 mmol), and HOBt (405 mg, 3 mmol) were stirred in $CHCl_3$ for 24 hours, then the reaction mixture was concentrated and purified by column chromatography (SiO_2: CH_2Cl_2/CH_3OH = 100: 1) to yield **11** as a white solid (281 mg, 66%). Mp: 181-183 °C; ^{1}H NMR (500 M, $CDCl_3$, δ): 1.44-1.50 (m, 2H), 1.71-1.79 (m, 4H), 2.20-2.21 (t, 1H, J = 2.5 Hz), 2.22-2.25 (t, 2H, J = 7.5 Hz), 4.04-4.06 (m, 2H), 4.16-4.19 (t, 2H, J = 2.5 Hz), 7.84-7.86 (t, 1H, J = 8.5 Hz), 8.04-8.06 (d, 1H, J = 8.5 Hz), 8.41-8.43 (d, 1H, J = 8.5 Hz), 8.58-8.59 (d, 1H, J = 8.5 Hz), 8.66-8.67 (d, 1H, J = 8.5 Hz); ^{13}C NMR (125 M, $CDCl_3$, δ): 25.06, 26.51, 27.58, 20.19, 36.17, 40.21, 71.55, 79.70, 122.27, 123.14, 128.13, 129.07, 130.34, 130.71, 131.15, 131.30, 132.11, 133.35; HRMS calc. for $[C_{21}H_{19}BrN_2O_3+H]^+$: 429.0637; Found: 429.0622.

Synthesis of 12: Compound **11** (426 mg, 1 mmol)**,** ethylenediamine (600 mg, 10 eq) were refluxed in ethanol for 48 hours. The reaction mixture was then concentrated, washed with water, and purified by column chromatography (SiO_2: CH_2Cl_2/CH_3OH =

10: 1) to yield **12** as yellow solid (401 mg, 23%). Mp. 98-100 °C; ^{1}H NMR (400 M, $CDCl_3$, δ): 1.75-1.81 (m, 2H), 2.22-2.23 (t, 1H, J = 6.4 Hz), 2.25-2.28 (t, 2H, *J* = 7.2 Hz), 3.20-3.23 (t, 2H, *J* = 7.2 Hz), 3.20-3.23 (t, 2H, *J* = 5.6 Hz), 3.43-3.47 (m, 2H), 3.52 (s, 2H), 4.06-4.08 (m, 2H), 4.17-4.21 (t, 2H, *J* = 5.6 Hz), 6.73-6.75 (d, 1H, *J* = 8.4 Hz), 7.64-7.68 (t, 1H, *J* = 8.4 Hz), 8.20-8.22 (d, 1H, *J* = 8.8 Hz), 8.48-8.50 (d, 1H, *J* = 8.4 Hz), 8.61-8.63 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (125 M, DMSO, δ): 25.41, 26.73, 27.97, 28.19, 35.43, 46.76, 73.18, 81.84, 104.19, 108.03, 120.50, 122.18, 124.50, 128.95, 129.75, 130.95, 134.54, 151.20, 163.27, 164.12, 172.30; HRMS calc. for. $[C_{23}H_{27}N_4O_3]^+$ ($M+H^+$): 407.2083; Found: 407.2071.

Synthesis of N5: Compound **12** (406 mg, 1 mmol), cholesterol-5-ene-3-beta-y chloroformate (449 mg, 1mmol) and 1 mL Et_3N were stirred for 24 hours, then the mixture was concentrated and purified by column chromatography (SiO_2: CH_2Cl_2/CH_3OH = 50: 1) to yield **N5** as a yellow solid (357 mg, 49%). Mp: 165-167 °C; ^{1}H NMR (500 M, $CDCl_3$, δ): 0.67 (s, 3H), 0.86 (d, 3H, *J* = 2 Hz), 0.87-0.88 (d, 3H, *J* = 2 Hz), 0.91-2.03 (m, 40H), 2.19-2.20 (t, 1H, *J* = 2.5 Hz), 2.23-2.26 (t, 2H, *J* = 7.5 Hz), 3.48-3.49 (t, 2H, *J* = 4.5 Hz), 3.68 (s, 2H), 4.04-4.06 (m, 2H), 4.14-4.17 (t, 2H, *J* = 7.5 Hz), 4.45-4.55 (m, 1H), 5.36 (m, 1H), 6.59-6.60 (d, 1H, *J* = 8.5 Hz), 7.63-7.66 (t, 1H, *J* = 8.5 Hz), 8.24-8.26 (d, 1H, *J* = 8. 5 Hz), 8.44-8.45 (d, 1H, *J* = 8 Hz), 8.57-8.55 (d, 1H, *J* = 8 Hz); ^{13}CNMR (125M, DMSO, δ): 11.88, 14.13, 18.75, 19.30, 21.07, 22.59, 22.71, 22.84, 23.86, 24.30, 25.07, 26.43, 27.56, 28.04, 28.24, 29.16, 29.37, 29.72, 31.87, 35.81, 36.16, 36.21, 36.59, 36.94, 38.52, 39.55, 39.69, 39.75, 39.86, 42.34, 50.05, 56.18, 56.73, 71.43, 75.48, 79.82, 103.45, 109.87, 120.41, 122.77, 124.80, 127.10, 129.80, 131.18, 134.61, 139.57, 150.13, 158.72, 164.82, 172.81. HRMS calc. for $[C_{51}H_{70}N_4O_5+H]^+$: 819.5424; Found: 819.5417.

1.6 Synthesis of N6



Scheme S6 Synthesis procedure of **N6**

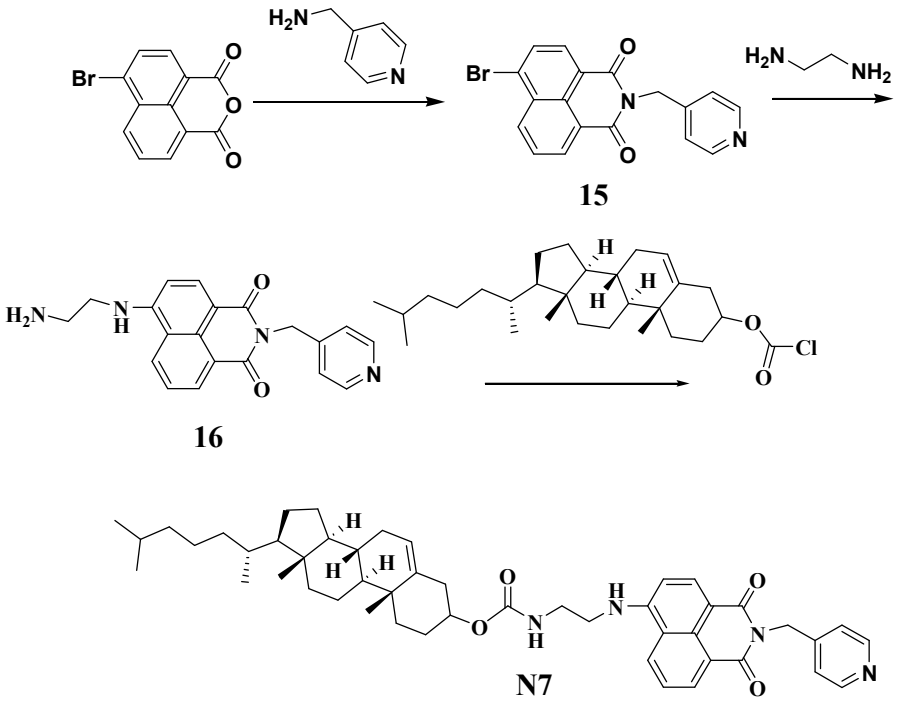
Synthesis of 13: 4-Br-1, 8-naphthalic anhydride (277 mg, 1 mmol) and 2-pyridinemethanamine (366 mg, 1 mmol) were refluxed in ethanol for 8 hours, the reaction mixture was concentrated and crystalized by ethanol twice, pale yellow solid was obtained (73.2 mg, 20%). Mp: 185-187 °C; ^{1}H NMR (400 M, $CDCl_3$, δ): 5.54 (s, 2H), 7.12-7.15 (t, 1H, J = 5.5 Hz), 7.32-7.33 (d, 1H, J = 8 Hz), 7.61-7.64 (m, 1H), 7.85-7.88 (m, 1H), 8.05-8.07 (d, J = 7.5 Hz), 8.44-8.46 (d, J = 8 Hz, 1H), 8.5 (d, J = 4.5 Hz, 1H), 8.60 (m, 1H), 8.68 (m, 1H); ^{13}C NMR (125 M, $CDCl_3$, δ): 45.27, 121.72, 122.29, 123.14, 128.24, 129.35, 130.62, 130.83, 131.26, 131.69, 132.52, 133.59, 136.64, 149.72, 156.15, 163.80; HRMS calc. for $[C_{18}H_{11}BrN_2O_2+H]^+$: 367.0082, 369.0062; Found: 367.0072, 369.0051.

Synthesis of 14: Compound **13** (426 mg, 1 mmol)**,** ethylenediamine (600 mg, 10 eq) were refluxed in ethanol for 48 hours, the reaction mixture was then concentrated,

washed with water and purified by column chromatography (SiO_2: CH_2Cl_2/CH_3OH = 10: 1) to yield **14** as a yellow solid (156 mg, 45%); Mp:223-225 °C; ^{1}H NMR (400 M, $CDCl_3$, δ): 3.18-3.21 (t, *J* = 6 Hz, 2H), 3.42-3.46 (t, 2H, *J* = 6 Hz), 5.55 (s, 2H), 6.72-6.74 (d, *J* = 8.4 Hz, 1H), 7.12-7.15 (m, 1H), 7.31(t, 1H, *J* = 8.4 Hz), 7.59-7.64 (m, 2H), 8.19-8.21(d, *J* = 8.4 Hz, 1H), 8.48-8.50 (d, *J* = 8.4 Hz, 1H), 8.54-8.56 (d, *J* = 4.8 Hz, 1H), 8.59-8.61 (d, *J* = 7.2 Hz, 1H); HRMS calc. for $(C_{20}H_{18}N_4O_2+H)^+$: 347.1598; Found: 347.1508.

Synthesis of N6: Compound **14** (346 mg, 1 mmol), cholesterol-5-ene-3-beta-yl chloroformate (449 mg, 1 mmol) and 1 mL Et_3N were stirred in $CHCl_3$ for 24 hours, then the mixture was concentrated and purified by column chromatography (SiO_2: CH_2Cl_2/CH_3OH = 50: 1) to yield **N6** as a yellow solid (326 mg, 43%). Mp: 272-274 °C; ^{1}H NMR (400 M, $CDCl_3$, δ): 0.68 (s, 3H), 0.86 (d, 3H, *J* = 2 Hz), 0.87-0.88 (d, 3H, *J* = 2 Hz), 0.91-0.92 (d, 3H, *J* = 6.5 Hz), 0.99-2.37 (m, 31 H), 3.48-3.49 (t, 2H, *J* = 5.5 Hz), 3.66-3.69 (t, 2H, *J* = 5.5 Hz), 4.55-4.62 (m, 1H), 5.37 (m, 1H), 5.53 (s, 2H), 6.58-6.60 (d, 1H, *J* = 8.5 Hz), 7.02-7.03 (m, 1H), 7.10-7.13 (t, 1H, *J* = 8.5 Hz), 7.57-7.62 (m, 2H), 8.24-8.25 (d, 1H, *J* = 8 Hz), 8.44-8.46 (d, 1H, *J* = 8 Hz), 8.53-8.54 (d, 1H, *J* = 8 Hz), 8.56-8.57 (d, 1H, *J* = 8 Hz); ^{13}C NMR (125 M, $CDCl_3$, *δ*): 12.01, 18.59, 19.44, 21.19, 22.71, 22.97, 23.98, 24.43, 28.17, 29.84, 32.07, 35.94, 36.33, 36.72, 37.06, 38.63, 39.67, 39.87, 39.98, 42.47, 45.11, 46.58, 50.17, 56.29, 56.85, 58.63, 75.59, 103.64, 109.89, 120.61, 121.51, 122.06,122.74, 122.96, 124.94, 127.38, 130.14, 131.57,135.05, 136.67, 139.69, 149.44, 150.47, 157.34, 158.74, 164.30, 164.99; HRMS calc. for $[C_{48}H_{62}N_4O_4+H]^+$: 759.4849; Found: 759.4844.

1.7 Synthesis of N7



Scheme S7 Synthesis procedure of **N7**

Synthesis of 15: 4-Br-1, 8-naphthalic anhydride (277 mg, 1 mmol) and 2-pyridinemethanamine (366 mg, 1 mmol) were refluxed in ethanol for 8 hours, the reaction mixture was concentrated and crystalized by ethanol twice, pale yellow solid was obtained (138 mg, 36%). Mp: 173-175 °C; ^{1}H NMR (400M, $CDCl_3$, δ): 5.36 (s, 2H), 7.37-7.38 (d, J = 5.2 Hz, 2H), 7.85-7.89 (t, J = 7.6 Hz, 1H), 8.05-8.07 (d, J = 7.6 Hz, 1H), 8.42-8.44 (d, J = 8 Hz, 1H), 8.55-8.56 (d, J = 4.8 Hz, 2H), 8.60-8.62 (d, J = 8.4 Hz, 1H), 8.67-8.69 (d, J = 7.2 Hz, 1H); HRMS calc. for $[C_{18}H_{11}BrN_2O_2+H]^+$: 367.0082, 369.0062; Found: 367.0072, 369.0051.

Synthesis of 16: Compound **15** (426 mg, 1 mmol)**,** ethylenediamine (600 mg, 10 eq) were refluxed in ethanol for 48 hours, the reaction mixture was then concentrated and washed with water. The filtrate was purified by column chromatography (SiO_2: CH_2Cl_2/CH_3OH = 10: 1) to yield **16** as a yellow solid (173 mg, 50%). Mp: 217-219 °C; ^{1}H NMR (500 M, DMSO, δ): 2.86-2.85 (t, J = 6 Hz, 2 H), 3.38-3.40 (t, 2H, J = 6 Hz), 5.23 (s, 2H), 6.83-6.86 (d, J = 8.8 Hz, 1H), 7.25-7.27 (d, J = 4.4 Hz, 2H), 7.69-7.89 (t, J = 8.4 Hz, 1H), 8.27-8.29 (d, J = 8 Hz, 1H), 8.42-8.44 (d, 1H, J =

8 Hz), 8.46-8.47 (d, *J* = 4.4 Hz, 2H), 8.75-8.77 (d, *J* = 8 Hz, 1H); ^{13}C NMR (125 M, DMSO-d_6): 43.66, 47.66, 47.79, 105.86, 108.98, 122.07, 123.36, 123.93, 126.15, 130.95, 131.50, 132.86, 136.45, 148.69, 151.48, 153.05, 164.68, 165.69; HRMS calc. for $[C_{20}H_{18}N_4O_2+Na]^+$: 369.1327; Found: 369.0063.

Synthesis of N7: Compound **16** (346 mg, 1 mmol), cholesterol-5-ene-3-beta-yl chloroformate (449 mg, 1 mmol) and 1 mL Et_3N were stirred in dry DMF for 24 hours, then the mixture was concentrated and purified by column chromatography (SiO_2: CH_2Cl_2/CH_3OH = 50: 1) to yield **N7** as a yellow solid (114 mg, 15%). Mp: 163-165 °C; ^{1}HNMR (500 M, DMSO, δ): 0.67 (s, 3H), 0.86 (d, *J* = 2.5 Hz, 3H), 0.87-0.88 (d, *J* = 2.5 Hz, 3H), 0.91-2.37 (m, 34 H), 3.48-3.49 (t, *J* = 3.5 Hz, 2H), 3.72-3.73 (t, *J* = 3.5 Hz, 2 H), 4.56-4.62 (m, 1H), 5.15-5.18 (m, 1H), 5.36 (s, 2H), 6.59-6.61 (d, *J* = 8.5 Hz, 1H), 7.35-7.36 (d, *J* = 6 Hz, 2H), 7.65-7.68 (t, *J* = 8.0 Hz, 1H), 8.27-8.29 (d, *J* = 8.5 Hz, 1H), 8.46-8.47 (d, *J* = 8.5 Hz, 1H), 8.51-8.52 (d, *J* = 6Hz, 2H), 8.60 (d, *J* = 7.0 Hz, 1H); ^{13}CNMR (125 M, DMSO-d_6): 11.98, 14.97, 18.56, 18.85, 19.42, 19.45, 21.16, 22.69, 22.95, 23.46, 23.96, 24.41, 28.21, 32.03, 34.61 35.91, 36.37, 36.69.36.84, 37.06, 38.63, 39.65,39.85, 42.44, 43.41, 46.66, 50.14, 56.27, 56.81, 58.51, 103.69, 109.35, 120.63, 122.95, 123. 30, 124.98, 127.80, 130.15, 146.94, 150.71, 151.48, 156.44, 158.90, 164.13, 164.86; $[C_{48}H_{62}N_4O_4+H]^+$: 759.4849; Found: 759.4856.

2. Gelation properties of N1-N7

Table S1 The gelation properties of **N1**- **N3** in different organic solvents by a heating-cooling (H-C) process or sonication (with concentration of 25 mg/mL).

Solvent	N1		N2		N3	
	H-C	sonication	H-C	sonication	H-C	sonication
methanol	P	P	P	P	P	P
ethanol	P	P	P	P	P	**G(22.5)**
benzene	S	S	S	S	P	P
isopropanol	P	P	P	P	P	P
propanol	P	P	S	P	P	P
toluene	P	P	S	S	S	P
acetone	P	P	S	S	P	P
Ethyl acetate	I	I	S	S	S	**G(15)**
$CHCl_3$	S	S	S	S	S	S
CH_2Cl_2	S	S	S	S	S	S

Note: P, precipitate; S, solution, I, insoluble, G, gel (critical gelation concentration)

Table S2 The gelation properties of **N4-N7** in different organic solvents by a heating-cooling process or sonication (with concentration of 25 mg/mL)

Solvent	N4		N5		N6		N7	
	H-C	sonication	H-C	sonication	H-C	sonication	H-C	sonication
methanol	I	I	P	P	P	P	P	**G (16.5)**
ethanol	I	I	S	**G (20)**	P	P	P	**G (14.3)**
benzene	I	I	S	**G (22.5)**	P	**G (7.7)**	P	**G (20)**
isopropanol	I	I	S	S	P	P	P	P
propanol	P	**G (35)**	S	S	P	**G (11.1)**	S	S
toluene	I	I	S	P	P	P	P	P
acetone	I	I	S	P	I	I	I	I
Ethyl acetate	I	I	S	S	I	I	S	S
$CHCl_3$	S	S	S	S	S	S	S	S
CH_2Cl_2	S	S	S	S	S	S	S	S

Note: P, precipitate; S, solution, I, insoluble, G, gel (critical gelation concentration)

3. Studies on the spectroscopy, morphology and aggregation pattern

Table S3 The photophysical properties of **N3** and **N5** in different state

Compounds	λ_{abs} (nm)	λ_{em} (nm)	Φ_f (%)	t (ns)
N3 (solution in ethanol)	439	527	60.3	3.38
N3 (powder)	-	544	19.9	10.15
N3 (gel in ethanol)	439, 494	587	9.2	1.61
N5 (solution in ethanol)	437	531	58.0	9.37
N5 (powder)	-	545	5.34	4.47
N5 (gel in ethanol)	437	525	15.9	2.84

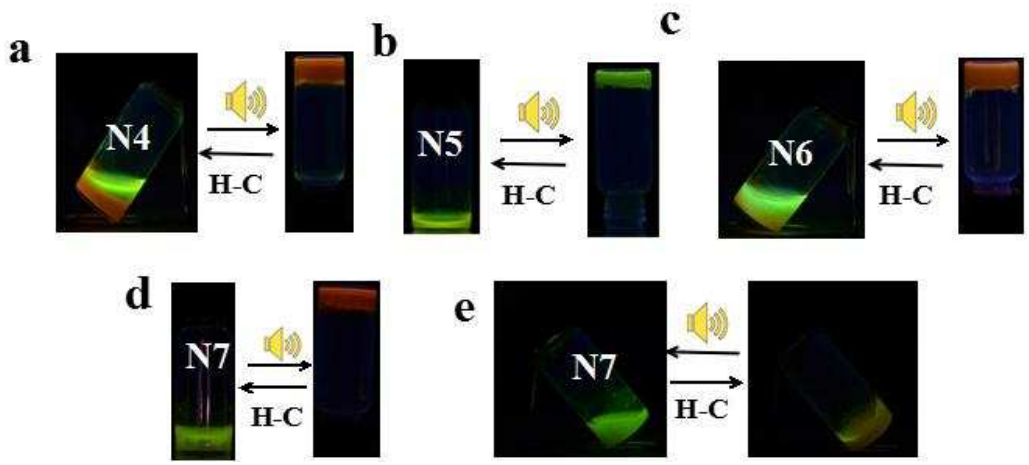


Figure S1 The reversible emission color changes of **N4**-**N7** in gelation. a) **N4** in propanol (35 mg/mL), partial-gel to gel formation; b) **N5** in ethanol (25 mg/mL), sol-to-gel formation; c) **N6** in propanol (25 mg/mL), precipitate-to-gel formation; d) **N7** in methanol (25 mg/mL), powder-to-gel formation; e) **N7** in ethanol (25 mg/mL), powder-to-gel formation.

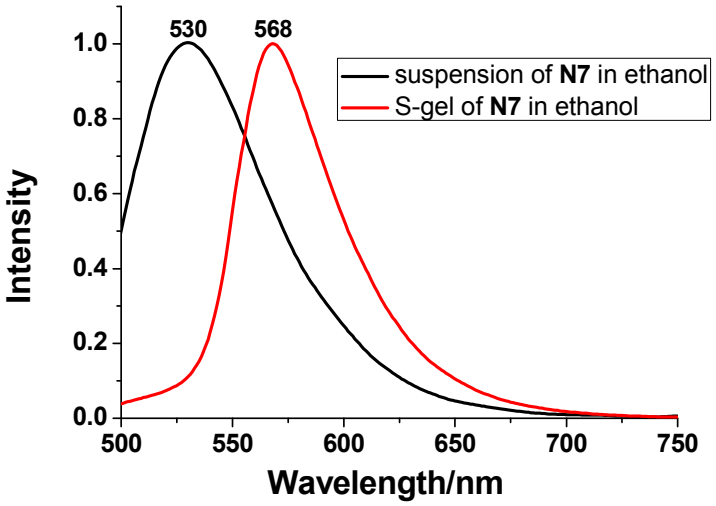


Figure S2 Uv-vis spectra of the suspension and S-gel of **N7** (25 mg/mL) in ethanol.

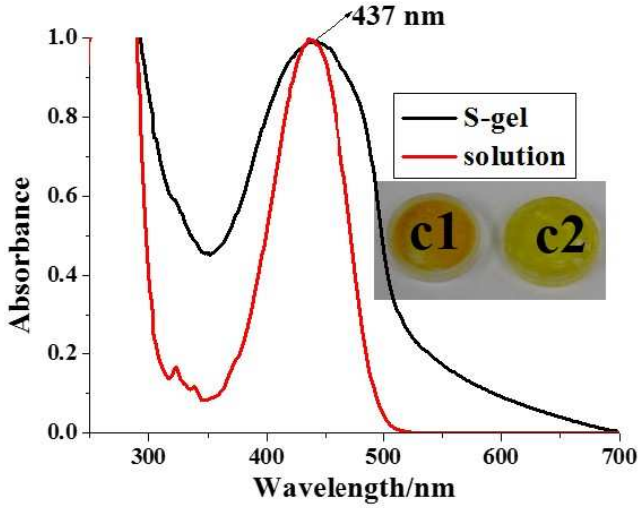


Figure S3 Uv-vis spectra of solution (10^{-4} M) and S-gel of **N5** in ethanol. Inset: C1, the powder obtained by evaporation; C2, S-xerogel.

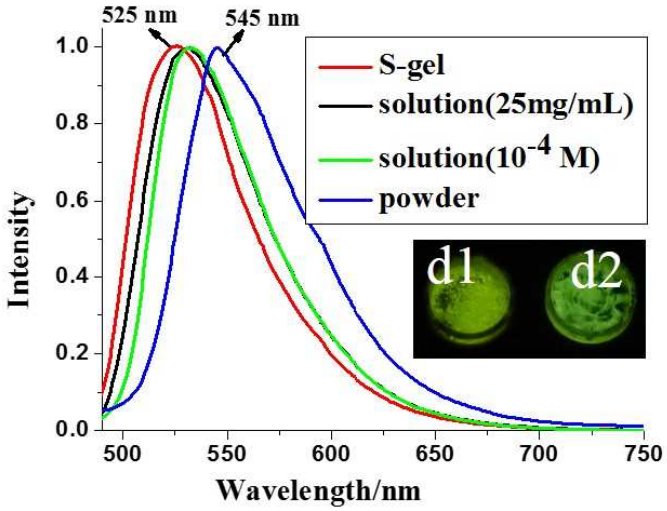


Figure S4 Fluorescence spectra of solution, powder (25 mg/mL, obtained by evaporation), S-gel and S-xerogels of **N5**. Inset: d1, the powder obtained by evaporation; d2, S-xerogel.

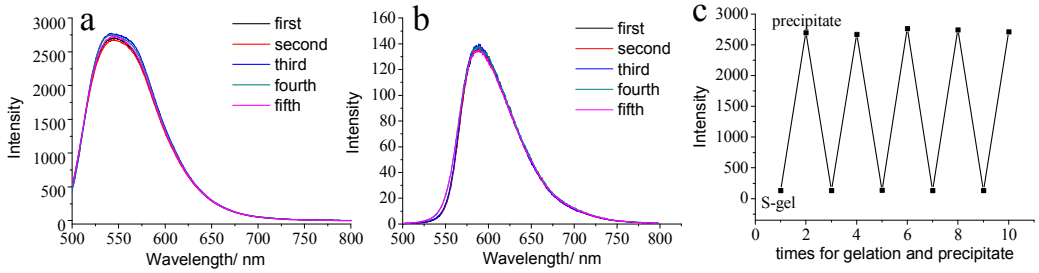


Figure S5 Emission spectra of **N3** (25 mg/mL in ethanol) via reversible (a) precipitate (obtained by a heating-cooling process) and (b) gel (sonication for 65 s) formation; (c) the fluorescence intensity of **N3** at 587 nm for the cycles of precipitate-to-gel transformation.

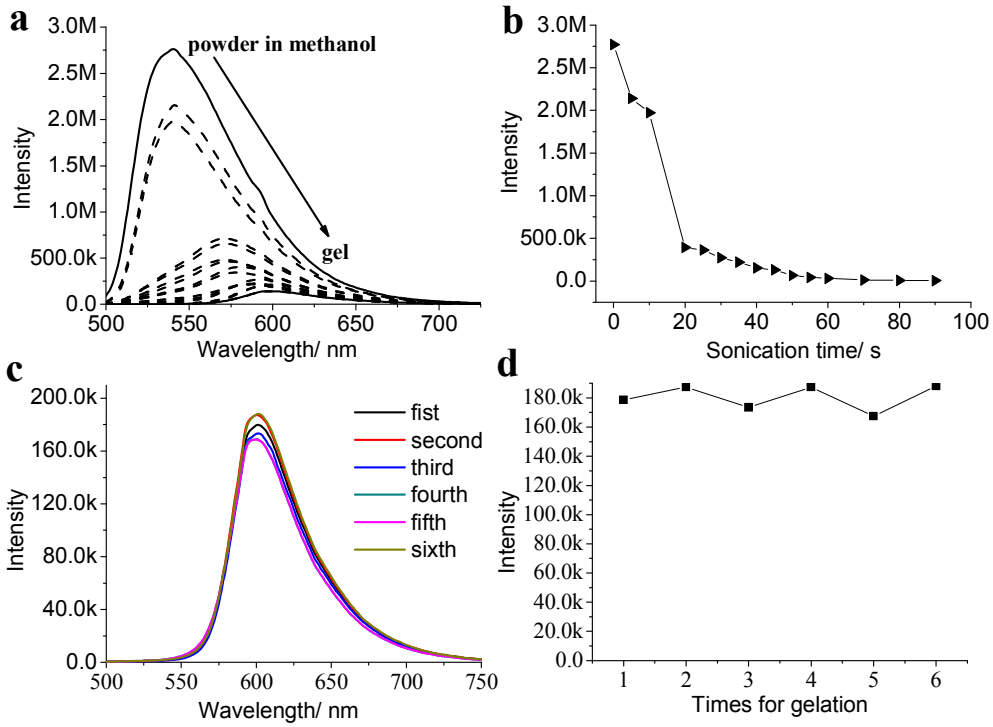


Figure S6 a) Emission spectra and b) emission intensity change at 540 nm of the assembly of **N7** (25 mg/mL) in methanol generated by sonication for various irradiation time; c) emission spectra of S-gels (25 mg/mL) of **N7** with the several times of reversible precipitate-to-gel transformation with aid of sonication for 2 min; d) the fluorescence intensity of **N7** S-gel at 595 nm for different cycles of precipitate-to-gel transformation.

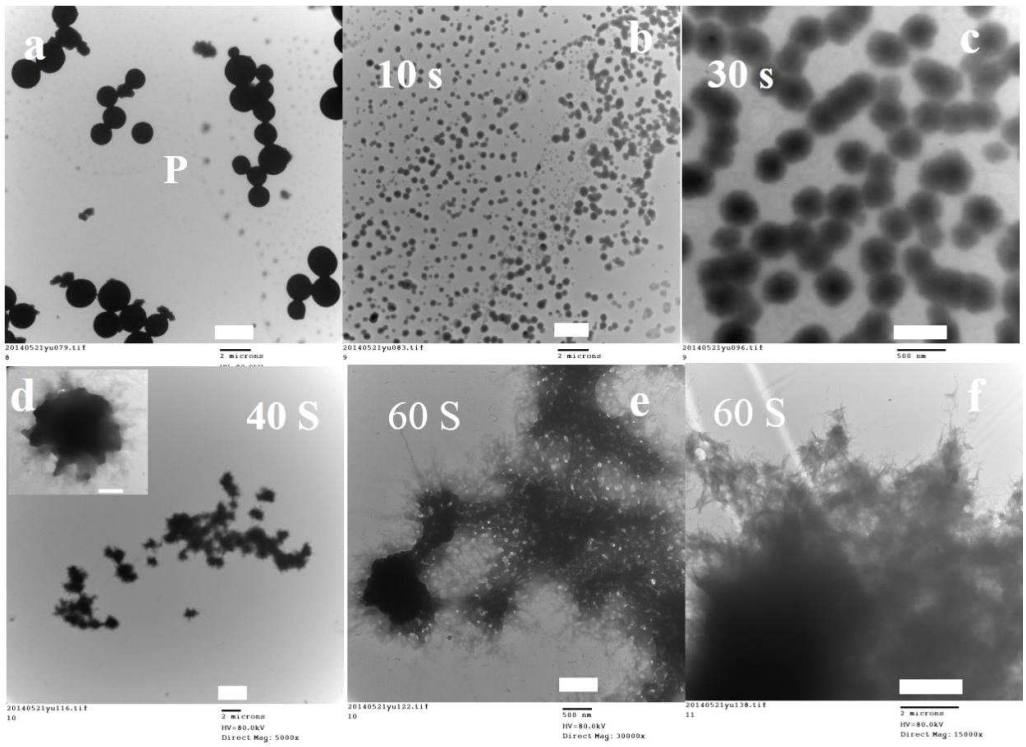


Figure S7 TEM images of precipitate-to-gel transitions of **N3** (25 mg/mL); a) precipitate; b) sonication for 10 s; c) sonication for 30 s; d) sonication for 40 s; e) sonication for 50 s; e) sonication for 60 s; f) the magnification picture of e). Scale bar: a) 2 μm; b) 2 μm; c) 500 nm; d) 2μm; insert picture, 500 nm; e) 500 nm; f) 2 μm.

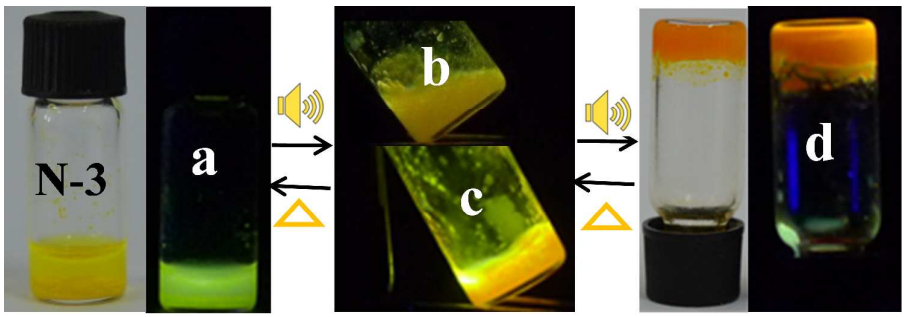


Figure S8 Photos of **N3** under ambient light and in dark upon irradiation of 365 nm. a) The precipitate of **N3** in ethanol, b) treated with sonication for 20 s (partial gel), c) 40 s (partial gel) and d) 60 s (gel).

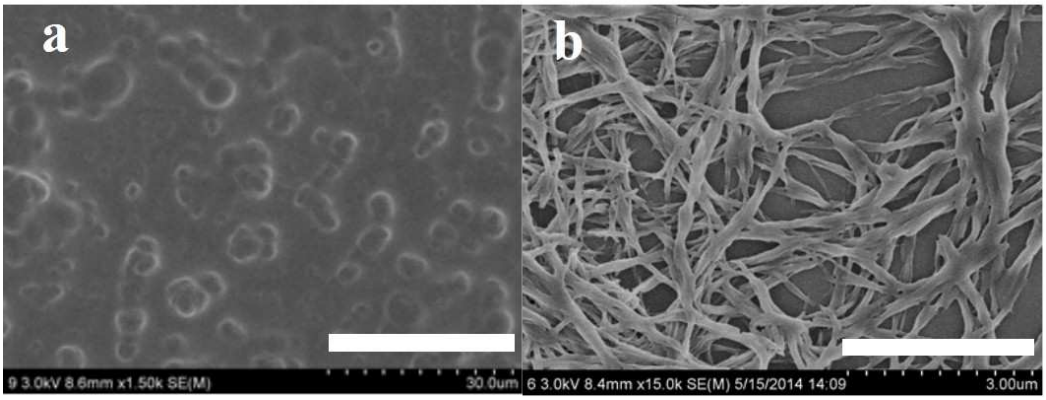


Figure S9 SEM images of **N5** assembly in ethanol. a) powder of **N5** obtained by evaporation method from ethanol (25 mg/mL); b) the S-gel of **N5** triggered by sonication for 3 min (25 mg/mL). Scale bar, a) 30 μm; b) 3 μm.

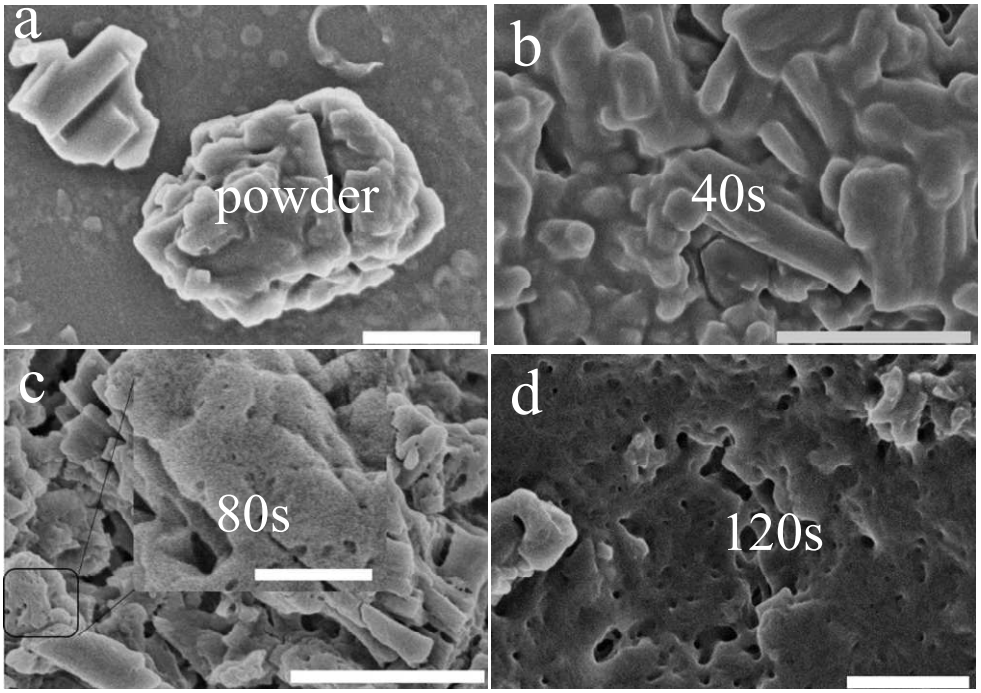


Figure S10 a) SEM images of powder of **N7**; b) treated with sonication for 40 s; c) treated with sonication for 80 s; d) treated with sonication for 120 s. Scale bar: a, 1 μm; b, 2 μm; c, 2 μm, d,1 μm; inset: 200 nm.

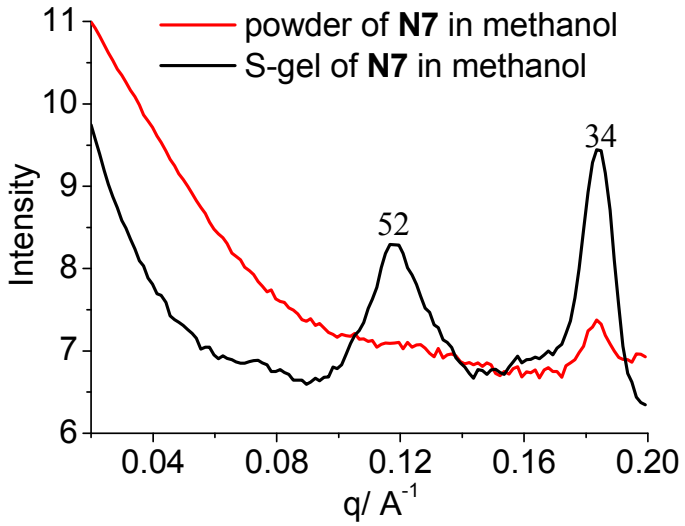


Figure S11 SAXS pattern of powder and S-xerogel of **N7** from methanol.

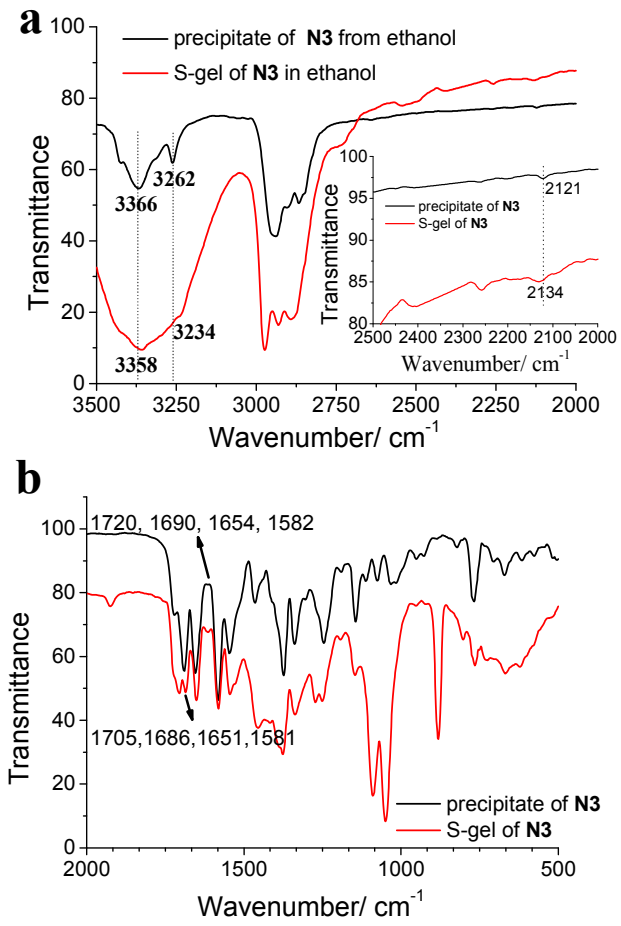


Figure S12 IR spectra of the precipitate and S-gel of **N3** (25 mg/mL).

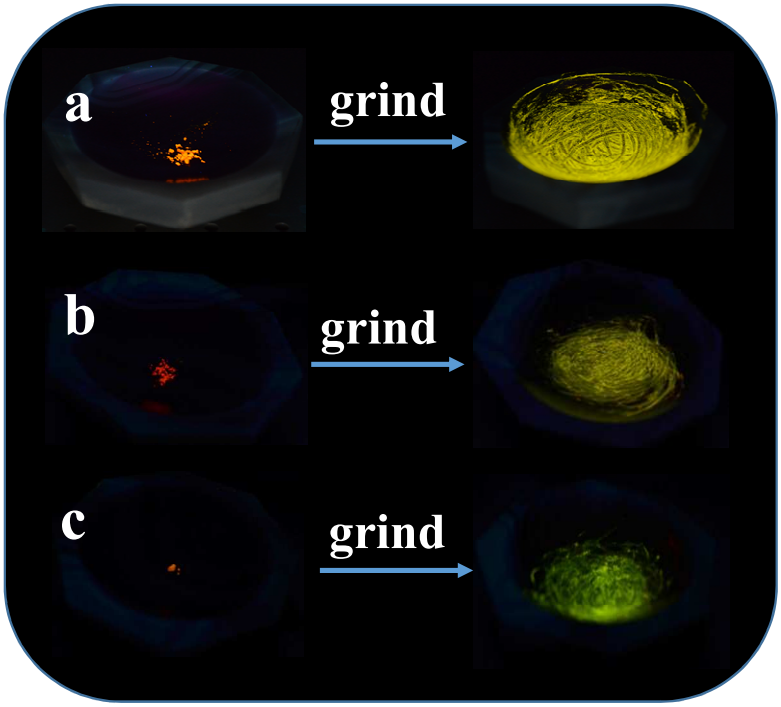


Figure S13 The color emission changes of xerogels after grinding in the dark upon irradiation at 365 nm. a) S-xerogel of **N3** from ethanol; b) S-xerogel of **N5** from propanol; c) S-xerogel of **N7** from methanol.

Figure S14 Apparatus (769YP-15A powder compressing machine) for the pressure sensing of S-xerogel of **N3**.

4. Life time studies of N3 at different states

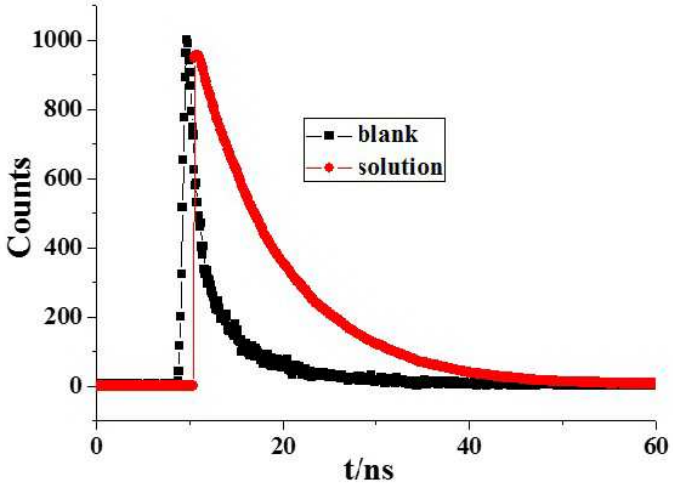


Figure S15 Fluorescence decay profiles of **N3** solution (10^{-4} M) in ethanol.

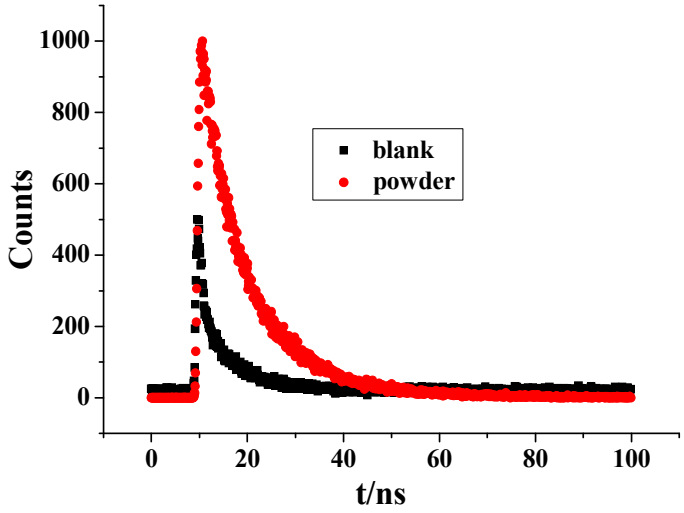


Figure S16 Fluorescence decay profile of **N3** powder from column.

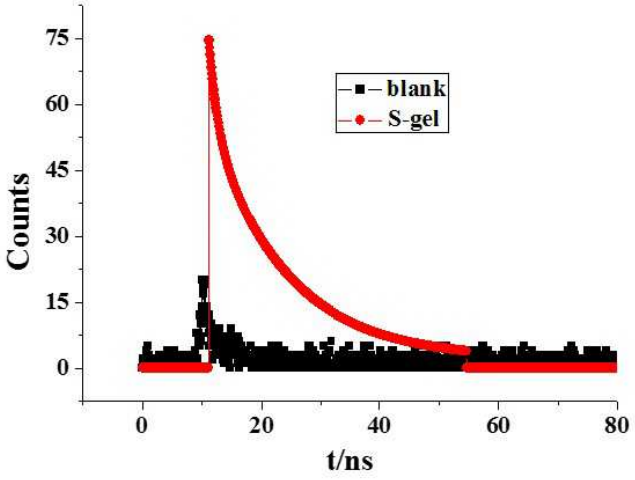


Figure S17 Fluorescence decay profile of **N3** S-gel in ethanol (25 mg/mL)

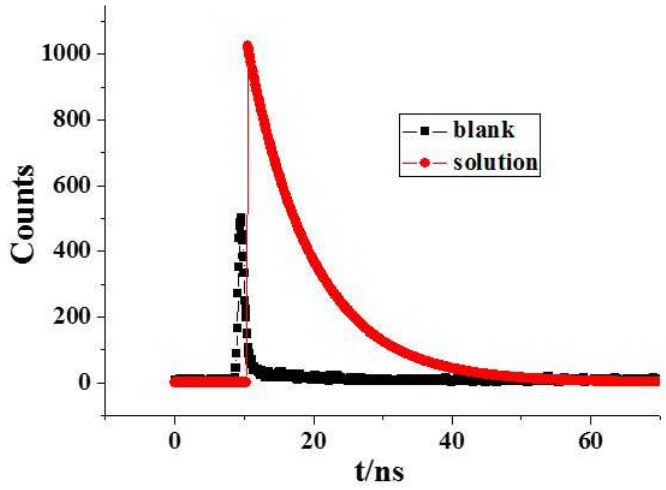


Figure S18 Fluorescence decay profile of **N5** (10^{-4} M) in ethanol

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