

Supplementary Information for

Detection of explosive vapors with a charge transfer molecule: Self-assembly assisted morphology tuning and enhancement in sensing efficiency

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1. Experimental Section

1.1. General

2,4-dinitrotoluene (DNT) was purchased from TCI and recrystallized from ethanol. 2,4,6-Trinitrotoluene was prepared from DNT using literature procedures.^{S1} All other chemicals were purchased from Aldrich, TCI or Wako and used as received. Air- and water-sensitive reactions were performed in argon atmosphere using standard Schlenk techniques. Melting points were determined with a Yanako NP-500P micro melting-point apparatus. ¹H and ¹³C NMR spectra were recorded on a 600MHz Bruker Avance DRX-600 Spectrometer. All the chemical shifts are referenced to (CH₃)₄Si (TMS; $\delta = 0$ ppm) for ¹H or residual CHCl₃ ($\delta = 77$ ppm) for ¹³C. High resolution mass spectra (HRMS) were obtained with SHIMADZU LCMS-IT-TOF workstation.

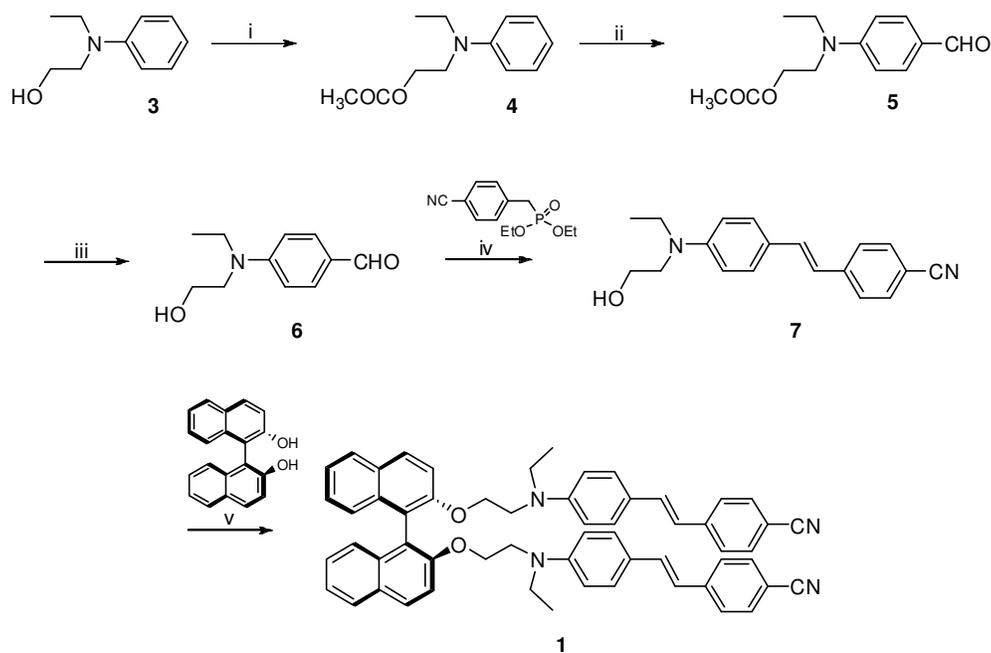
1.2. Measurements

Electronic absorption spectra were recorded on a Hitachi U-2900 spectrophotometer and the emission spectra were recorded on a Hitachi F-7000. Circular Dichroism (CD) measurements were carried out on a JASCO J-810 spectrophotometer. Optical properties in solution were measured by using a quartz cuvette with 1 cm or 1mm path length and quartz plates were used for studies in film state. For emission studies, right angle geometry was used for solutions in 1 cm cuvette, whereas, front face geometry used for film state and solutions in 1 mm cuvette. Fluorescence quantum yields were determined relative to quinine sulphate ($\Phi_f = 0.546$ in 0.1M H₂SO₄) using optically matching solutions. Solid-state fluorescence quantum efficiency was measured using a calibrated integrating sphere in a SPEX Fluorolog spectrofluorimeter. Xe-arc lamp was used to excite the thin-film sample placed in the sphere, with 390 nm as the excitation wavelength. Field-emission scanning electron microscopy (FE-SEM) observations of the samples were carried out using a Hitachi S-4800 at an accelerating

voltage of 10 kV. Fluorescent microscopic images were recorded on a Leica DM2500 fluorescence microscope using UV light (330-380 nm) as the excitation source.

Fluorescence quenching studies of **1** and **2** in film state by exposing to the explosive vapors (DNT and TNT) was done according to literature procedures.^{S2} 1.5 g of powdered DNT or TNT was placed in a 50 mL glass vial. Some cotton was placed over the powdered explosives to avoid direct contact with the film. The sealed glass vial was kept overnight to get constant, saturated vapor pressure inside. The fluorescence spectra of the films were measured immediately after exposing to the explosive vapors for a specific time.

1.3. Synthesis and Characterization



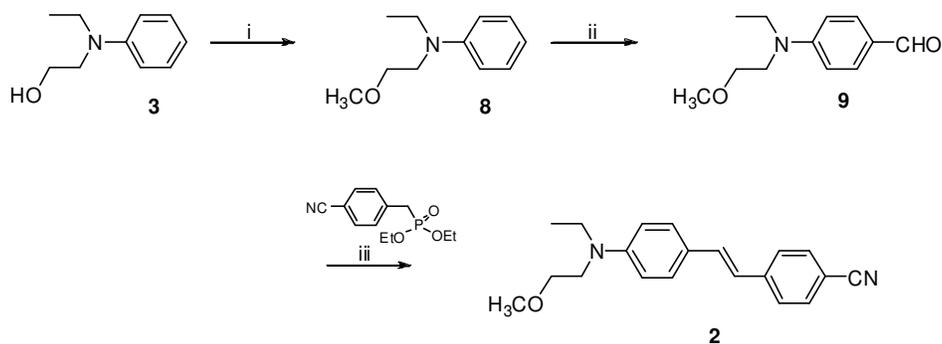
Scheme 1. Reagents and conditions: i) acetic anhydride, heat, 99%; ii) DCE, DMF, POCl₃, reflux, 92%; iii) MeOH, H₂O, NaOH, 95%; iv) KO^tBu, THF, 80%; v) PPh₃, THF, DIAD, Sonication, 65%.

Synthesis of **1** was achieved as per Scheme 1. 4-(*N*-ethyl-*N*-(2-hydroxyethyl)amino) benzaldehyde (**6**) was synthesized according to literature procedures.^{S3} Stilbene derivatives **7** was prepared in 80 % yield by the Wittig reaction between phosphonate ester of *p*-cyanobenzylbromide (2.1 g, 10 mmol, 1 eq.) with **5** (2.6 g, 10 mmol, 1 eq.) in anhydrous

THF (20 mL) in presence of KO^tBu (13.5 g, 12 mmol, 1.2 eq). The mixture was stirred for 1 h at 80 °C, cooled to room temperature and solvent was rotary evaporated. Addition of saturated NaHCO₃ solution yielded a yellow precipitate. Filtered and washed with water. Precipitate was then dissolved in CH₂Cl₂ and extracted with water. The organic phase was dried over anhydrous Na₂SO₄, filtered and evaporated to dryness. The residue was then purified by column chromatography (SiO₂, CHCl₃). Recrystallized from chloroform-hexane mixture to yield pure *trans*-isomer.

Modified Mitsunobu reaction reported by Lepore *et al.*^{S4} was used for the synthesis of stilbene appended binaphthyl derivative (**1**). (S)-(-)-1,1'-Bi(2-naphthol) (200 mg, 0.7 mmol, 1 eq.), stilbene derivative (512 mg, 1.75 mmol, 2.5 eq.), triphenylphosphine (460 mg, 1.75 mmol, 2.5 eq.) and anhydrous THF (2 mL) were taken in a glass vial and sonicated for 5 minutes giving a clear solution. While sonicating, diisopropylazodicarboxylate (0.35 mL, 1.75 mmol, 2.5 eq.) was added dropwise to the reaction mixture. Sonication was continued further for 15 minutes. The reaction mixture was then purified by column chromatography (SiO₂, CHCl₃). Final purification was carried out by recycling preparative GPC using chloroform as the eluent.

1: mp 192 °C; ¹H NMR (600 MHz, CDCl₃) δ (ppm): 0.68-0.73 (t, 6H), 2.56-2.67 (m, 4H), 3.22-3.24 (t, 4H), 4.02-4.04 (t, 4H), 6.32-6.34 (d, 4H), 6.77-6.80 (d, 2H), 7.05-7.08 (d, 2H), 7.15-7.17 (d, 2H), 7.21-7.23 (m, 6H), 7.33-7.35 (d, 4H), 7.48-7.50 (d, 4H), 7.56-7.58 (d, 4H), 7.86-7.88 (d, 2H), 7.92-7.94 (d, 2H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 11.6, 44.6, 49.2, 67.9, 110.8, 111.3, 115.5, 120.6, 121.5, 123.6, 123.9, 125.4, 126.1, 126.4, 127.9, 128.3, 129.4, 129.6, 130.2, 132.0, 132.4, 134.1, 142.9, 147.8, 154.2; FT-IR (KBr) ν_{max}: 744, 825, 963, 1185, 1270, 1354, 1458, 1521, 1590, 2222, 2870, 2924, 2968, 3017, 3058, 3171; HRMS (m/z): 834.3856 (calculated mass – 834.3934).



Scheme 2. Reagents and conditions: i) CH_3I , NaH , THF, reflux, 88%; ii) DCE, DMF, POCl_3 , reflux, 92%; iii) KO^tBu , THF, 92%;

Synthesis of **2** was achieved as per scheme 2. 2-Methoxyethylethylaniline (**8**) was prepared according to literature procedures.^{S5} Other steps were carried out similar to that of scheme 1.

2: mp 93 °C; ^1H NMR (600 MHz, CDCl_3) δ (ppm): 1.17-1.20 (t, 3H), 3.38 (s, 3H), 3.45-3.46 (q, 2H), 3.53-3.56 (m, 4H), 6.68-6.70 (d, 2H), 6.84-6.86 (d, 1H), 7.12-7.15 (d, 1H), 7.39-7.41 (d, 2H), 7.51-7.52 (d, 2H), 7.57-7.59 (d, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ (ppm): 12.5, 45.8, 50.3, 59.4, 70.7, 109.5, 112.0, 119.8, 122.0, 124.2, 126.5, 128.8, 132.7, 132.9, 143.3, 148.6; FT-IR (KBr) ν_{max} : 736, 824, 965, 1182, 1275, 1354, 1459, 1522, 1591, 2224, 2813, 2898, 2938, 2972, 3021, 3175; HRMS (m/z): 322.2087 (calculated mass – 322.2045).

2. Photophysical Properties

trans-Stilbene moiety readily isomerizes in solution when exposed to UV light but exposure to room light for short periods of time has little effect on the absorption spectrum. The isomerization effect was almost negligible in film state when exposed to room light and UV light for short periods.

Table S1. Summary of the Absorption and emission characteristics of **1** and **2** in different solvents with increasing polarity ($c = 1 \times 10^{-6}$ M, $l = 1$ cm).

| Compound | Solvent | Absorption | | Emission | |
|----------|------------|-----------------------|--|-----------------------|----------|
| | | λ_{\max} (nm) | $\epsilon \times 10^4$ ($M^{-1}cm^{-1}$) | λ_{\max} (nm) | Φ_f |
| 1 | Toluene | 391 | 4.78 | 455 | 0.053 |
| | Chloroform | 395 | 4.51 | 485 | 0.062 |
| | THF | 396 | 4.68 | 489 | 0.067 |
| | DCM | 397 | 3.48 | 497 | 0.078 |
| | DMF | 399 | 5.94 | 518 | 0.098 |
| 2 | Toluene | 390 | 2.63 | 454 | 0.056 |
| | Chloroform | 390 | 2.29 | 482 | 0.061 |
| | THF | 391 | 2.12 | 489 | 0.066 |
| | DCM | 392 | 1.43 | 496 | 0.076 |
| | DMF | 395 | 2.36 | 518 | 0.092 |

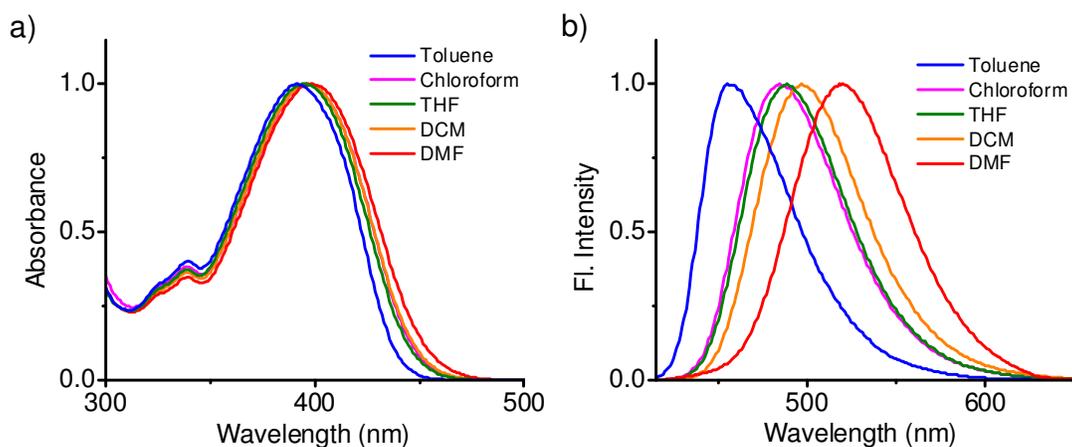


Figure S1. (a) Absorption and (b) emission spectra of **1** in different solvents at room temperature ($c = 1 \times 10^{-6}$ M, $l = 1$ cm).

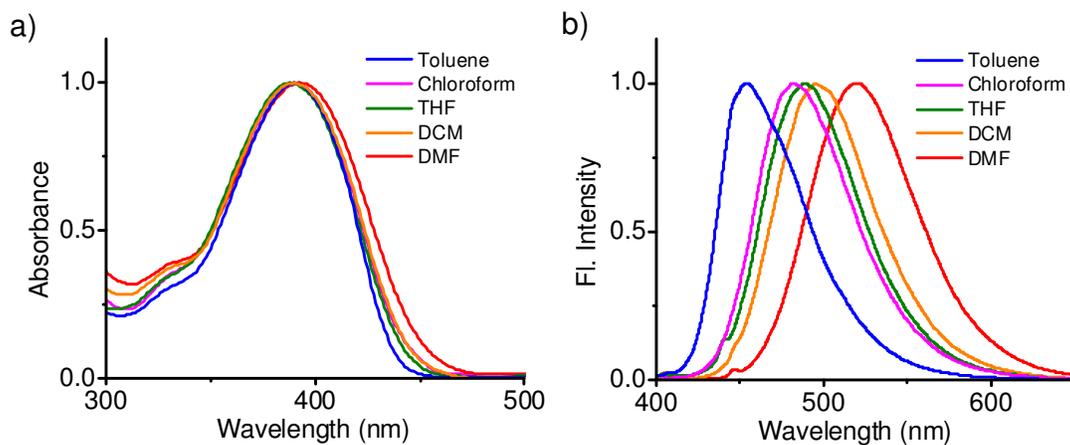


Figure S2. (a) Absorption and (b) emission spectra of **2** in different solvents at room temperature ($c = 1 \times 10^{-6}$ M, $l = 1$ cm).

Samples for the self-assembly studies were prepared by adding required amount of toluene to the chloroform solution keeping the concentration at 4×10^{-4} M followed by heating and cooling.

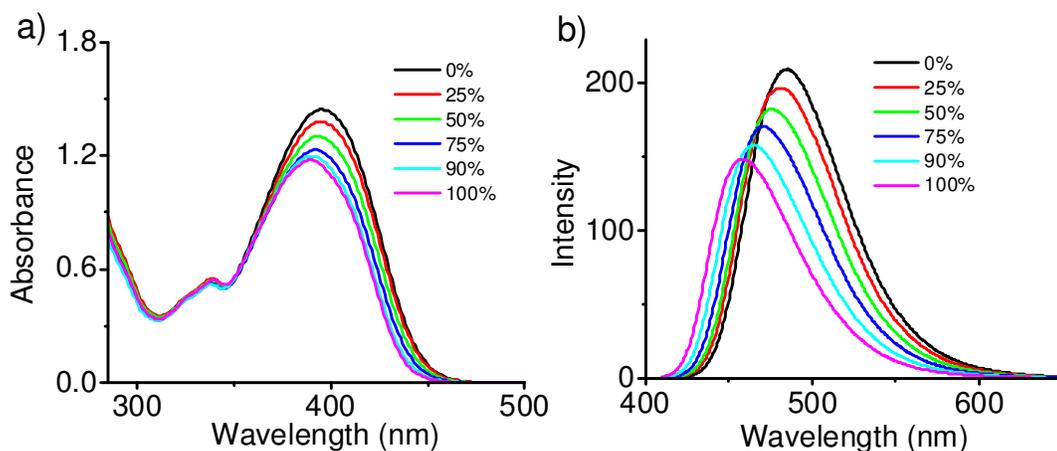


Figure S3. (a) Absorption and (b) emission spectral changes of **1** on addition of increasing amounts of toluene to the chloroform solution ($c = 4 \times 10^{-4}$ M, $l = 1$ mm).

Table S2. Fluorescence quantum yields of **1** and **2** in film state drop casted from solutions containing different volume % of chloroform and toluene. Sample solutions were prepared as explained above.

| Compound | Vol% of toluene in toluene-CHCl ₃ mixture from which film was prepared | Φ_f |
|----------|---|----------|
| 1 | 0 | 0.33 |
| | 50 | 0.31 |
| | 75 | 0.35 |
| | 90 | 0.32 |
| | 100 | 0.33 |
| 2 | 0 | 0.24 |
| | 50 | 0.25 |
| | 75 | 0.26 |
| | 90 | 0.21 |
| | 100 | 0.25 |

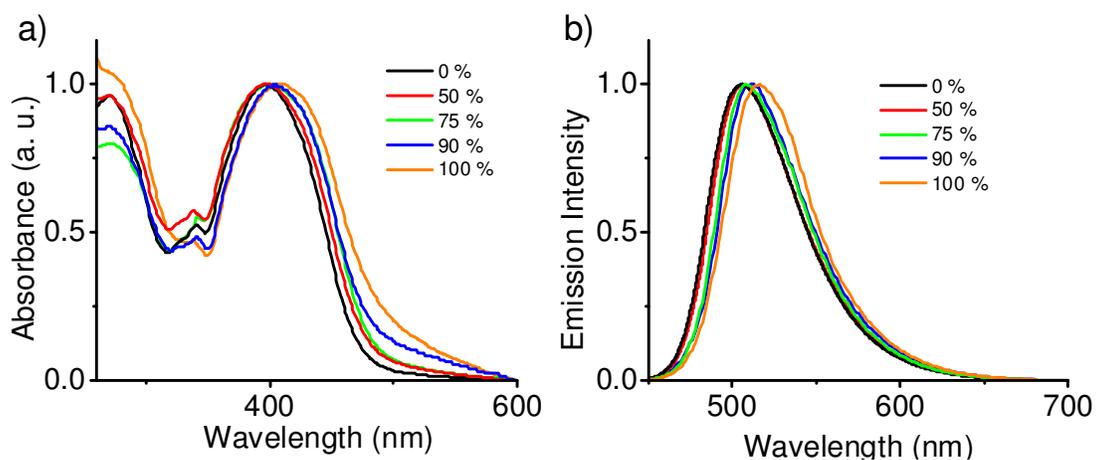


Figure S4. (a) Absorption and (b) emission spectra of **1** in film state drop casted from chloroform-toluene solution containing different amounts of toluene.

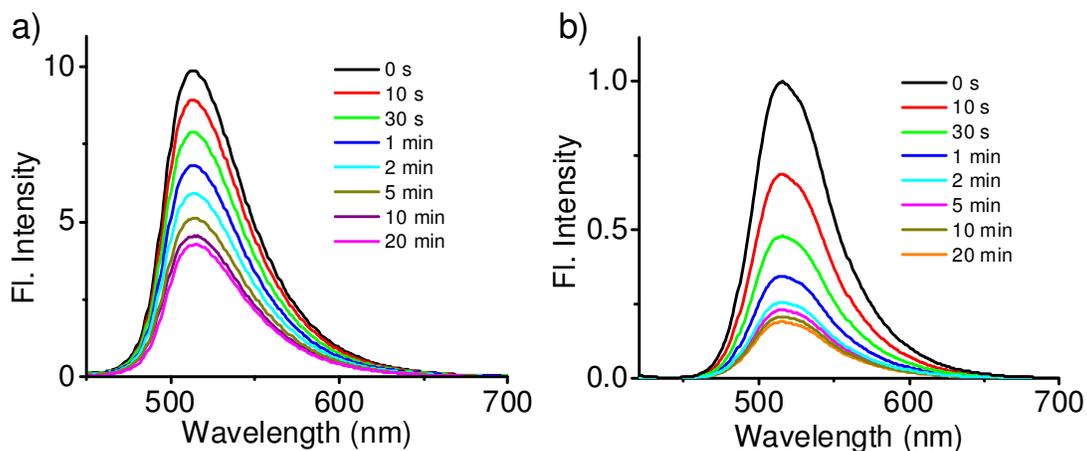


Figure S5. Fluorescence quenching of **1** in film state drop casted from (a) 1:9 v/v chloroform-toluene and (b) toluene solution on exposure to saturated vapor of DNT at different time.

3. SEM Analysis

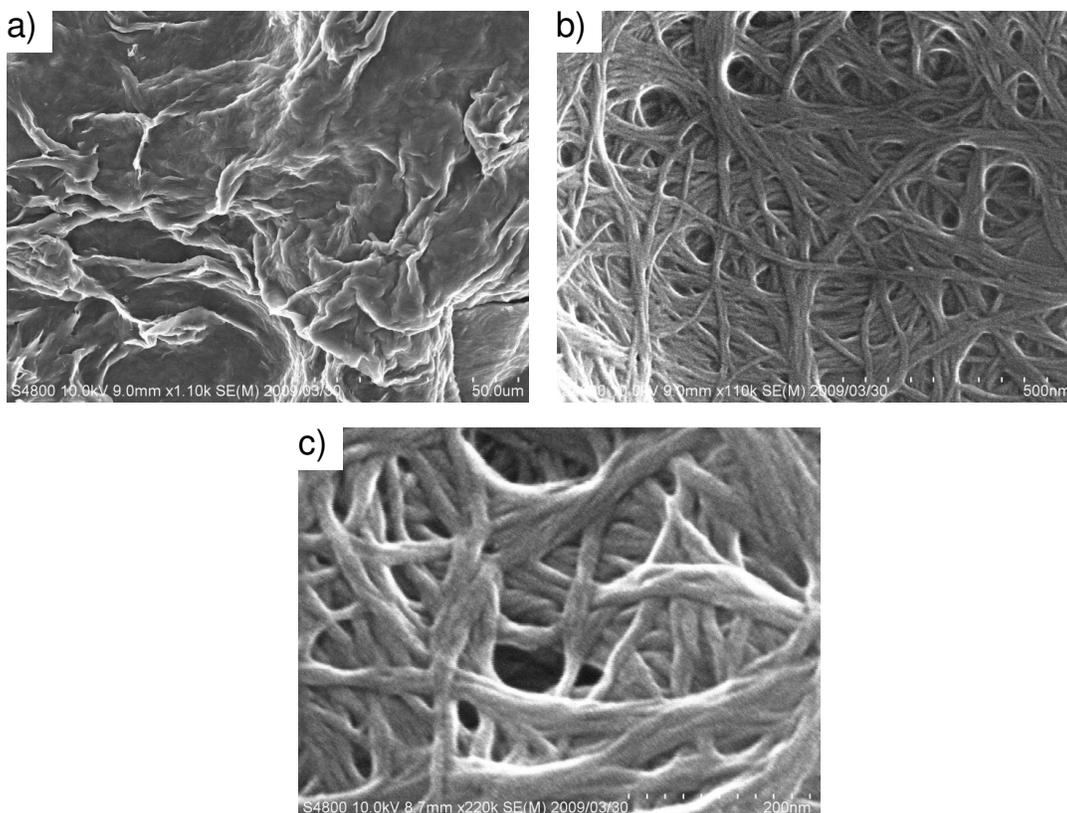


Figure S6. SEM images of **1** drop casted from 1:3 v/v chloroform-toluene mixture at different magnifications.

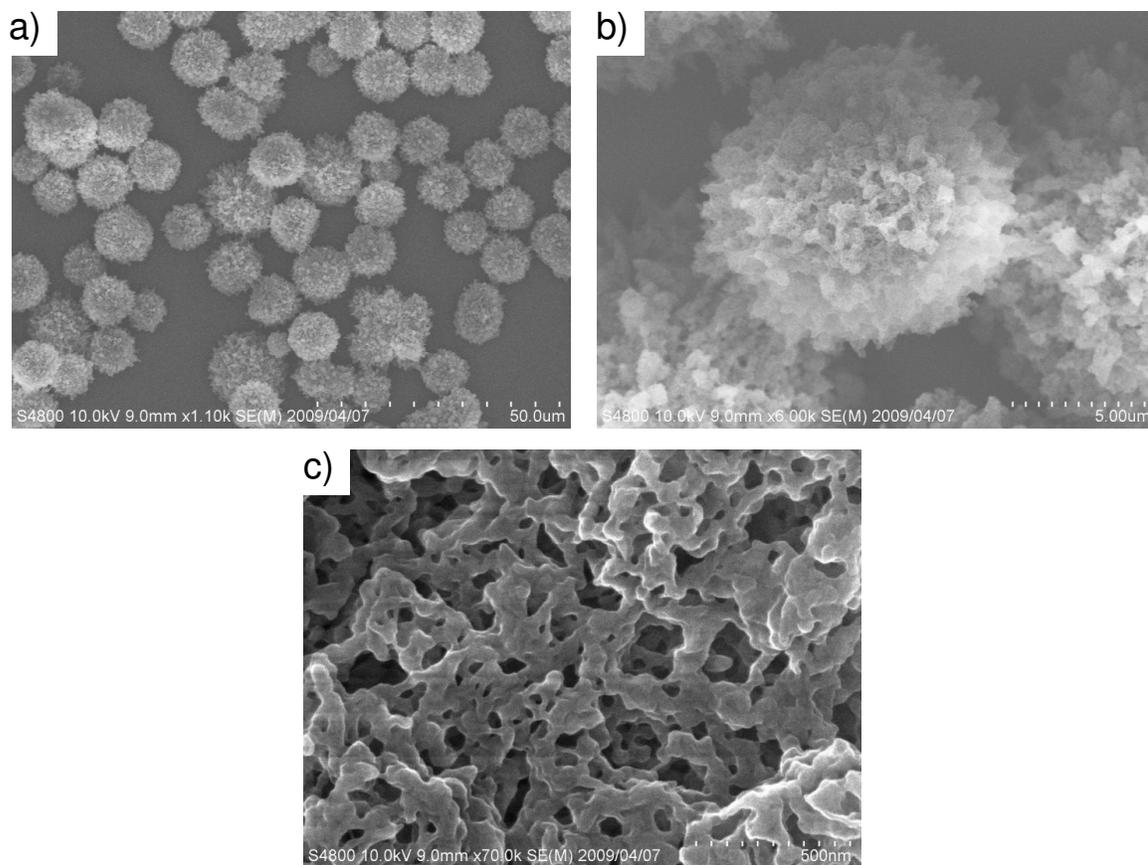


Figure S7. SEM images of **1** drop casted from toluene solution at different magnifications.

References

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