Supplementary Information

Solid-State Emissive Cyanostilbene Based Conjugated Microporous Polymers via Cost-Effective Knoevenagel Polycondensation

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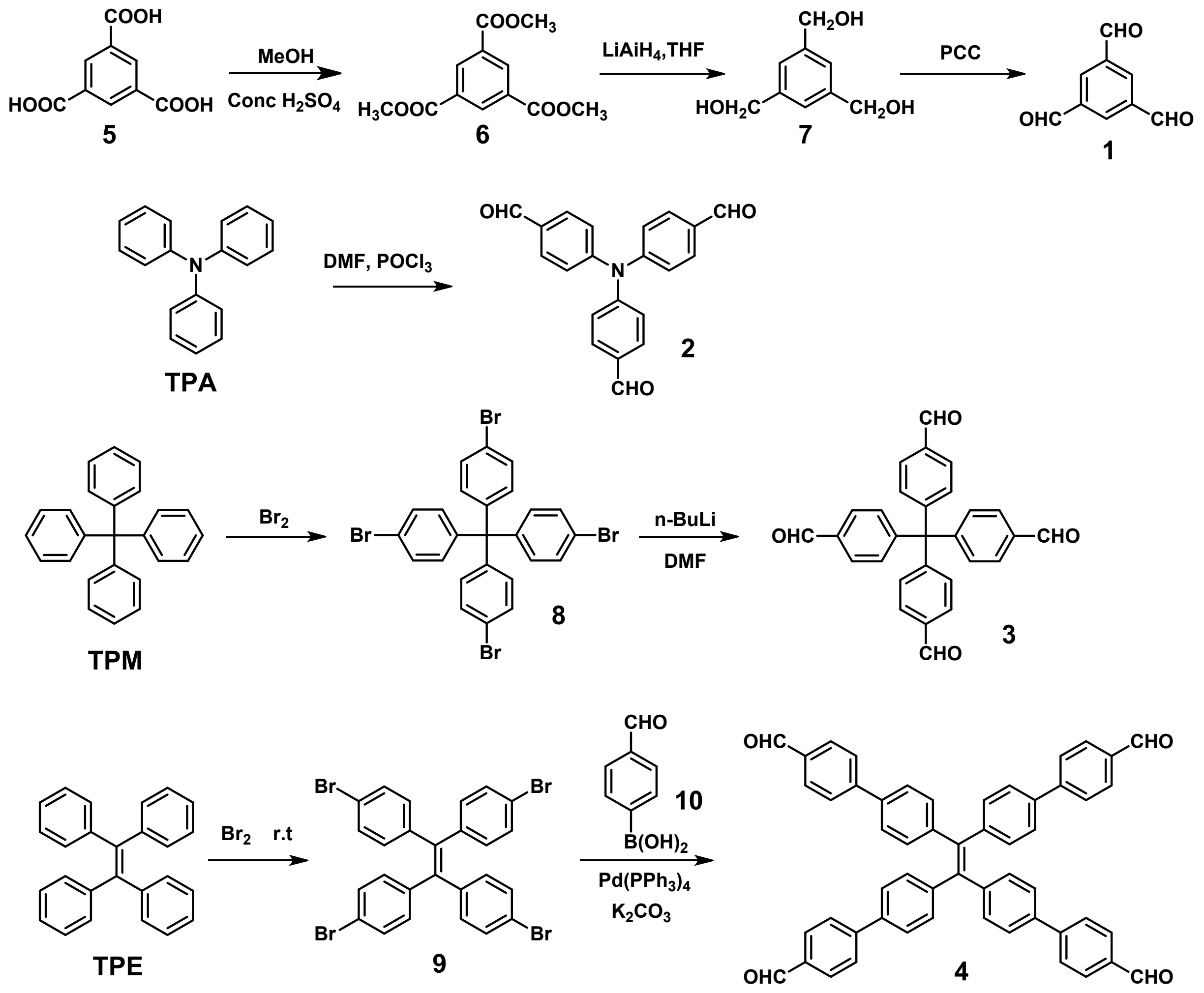
Section 1. Materials and Methods

Benzene-1,3,5-tricarboxylic acid, 1,1,2,2-tetraphenylethene, and tetraphenylmethane were purchased from Alfa Aesar. Triphenylamine was obtained from Sigma Aldrich. Pyridinium chlorochromate (PCC) was purchased from J&K Scientific and 4-formylphenylboronic acid was purchased from Acros. All the commercial chemicals were directly used without further purification unless otherwise noted. Solvents were purified according to standard procedures.

Liquid ^{1}H NMR spectra were recorded on a Bruker AVANCE III-400 spectrometer. The ^{13}C CP/MAS NMR spectra were recorded with the contact time of 2 ms (ramp 100) and a pulse delay of 3 s with a 4-mm double-resonance probe. The spinning rate was set as 10 KHz. FT-IR spectra were performed on a Bruker ALPHA spectrometer using KBr pellets in the frequency range of 500-4000cm^{-1}. Elemental analyses were measured by Elementar model Vario Micro analyzer. Field emission scanning electron microscopies (FE-SEM) were performed on a JEOL model JSM-6700 microscope operating at an accelerating voltage of 5.0 kV. The FE-SEM samples were prepared by adhering CMP powders to mica substrate using Conductive tape and then coated with gold. Transmission electron microscopies (TEM) and high resolution transmission electron microscopies (HR-TEM) were performed on a FEI model Tecani 20 microscope and a JEOL model JSM-2100F. The TEM samples were prepared by drop-casting a supersonicated methanol suspension of CMPs onto a copper grid. Powder X-ray diffraction (PXRD) measurement was carried out on X-ray diffractometer Rigaku model D/Max-2500 diffractometer at 40 kV, 100 mA with a Cu-target tube and a graphite monochromator. The diffuse reflectance spectra (Kubleka-Munk spectrum) were recorded on a SHIMADZU UV-3600 spectrometer equipped with integration sphere. Fluorescence spectra were recorded at 25 ^{o}C on a Hitachi model F-7000 spectrofluorometer and corrected for wavelength-dependent detector sensitivity and excitation light source output. The absolute fluorescence quantum yields were recorded by Steady-Transient Fluorescence Spectrometer model FLS920 produced by EDINBURGH. The excitation wavelengths were 400 nm, 480 nm, 452 nm, and 500nm for **Bn-CS-CMP**, **TPA-CS-CMP**, **TPM-CS-CMP**, and **TPE-CS-CMP** respectively. Quantum yields were determined according to published procedures.[S1] Solid-state tetraphenylethene was used as a calibration reference. The transient fluorescence decay curves were measured on the FLS 920 (EDINBURGH, UK). Lifetime data were obtained using a 405 nm laser excitation light source, which were then fitted using a tri-exponential model with better fitting qualities. Surface areas and pore size distributions were measured by nitrogen adsorption and desorption at 77.3 K using a Bel Japan Inc. model BELSOPR-mini II analyser and the samples were degassed at 150 ^{o}C for 3 h under vacuum (10^{-5} bar) before analysis. The pore size distribution was calculated from the adsorption branch with the nonlocal density functional theory (NLDFT).

Section 2. Synthetic procedures



Scheme S1. Synthetic routes of the four aldehyde monomers **1-4** with different molecular lengths, symmetry and electronic properties.

1,3,5-Benzenetricarboxylic acid trimethyl ester (6)

To a two-necked round bottom flask was added 1,3,5-benzenetricarboxylic acid **5** (8.0 g, 38 mmol), methanol(100 ml). Conc. H_2SO_4 (2.5 mL) was added slowly under ice bath after the 1,3,5-benzenetricarboxylic acid had been all dissolved in MeOH. The mixture was stirred at reflux for 20 h, white precipitate was formed after the mixture was cooled to room temperature, then saturated $NaHCO_3$ was added slowly until the PH≈7. The precipitate was collected by filtration, dried in vacuum, affording a colorless solid as the product **6** (9.03 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.86 (s, 3H), 3.99 (s, 9H).

1,3,5-Tris(hydroxymethyl)benzene (7)

To a two-necked round bottom flask containing $LiAlH_4$ (3.5 g, 92 mmol) was slowly added THF (30 ml) and the solution of **6** (7.0 g, 28 mmol) in THF (120 ml) at 0 °C. The mixture was then stirred and reflux for 20 h. After cooling to r.t., water (100 ml) was slowly added to the above mixture. The resulted residue was filtered off, and the filtrate (aqueous phase) was concentrated in vacuum, to afford **7** as a colorless solid (4.29 g, 92%). ^{1}H NMR (400 MHz, D_2O): δ (ppm) 7.27 (s, 3H), 4.61 (s, 6H).

1,3,5-Benzenetricarboxaldehyde (1)[S2]

To a two-necked round bottom flask was added **7** (3.3 g, 19.6 mmol), dichloromethane (180 ml) and pyridinium Chlorochromate complex (PCC, 12 g, 55.7 mmol) was added slowly to the above mixture under stirring. The mixture was stirred at room temperature for 20 h under nitrogen, then diluted with diethyl ether (80 ml) and keep for stirring for another half an hour. Then the mixture was filtered by celites and the filtration was concentrated under vacuum to give a black solid which was further purified by silica gel column chromatography (eluent: CH_2Cl_2). Compound **1** was obtained as a white solid (2.00 g, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 10.21 (s, 3H), 8.65 (s, 3H).

Tri(4-formylphenyl)amine (2)[S3]

To the mixture of phosphorus oxychloxide (37.4 mL, 401 mmol) and DMF (40.8 mL, 527 mmol) was added a solution of triphenylamine (**TPA**) (10 g, 40.1 mmol) in $CHCl_3$ (20 mL), then the mixture was stirred at 100 °C for 2 days. The mixture was poured into ice-water mixture, neutralized to pH≈7 with 5% NaOH aqueous solution, extracted with DCM. The organic phase was washed with water and brine, dried over $MgSO_4$, concentrated in vacuum. The residue was filtered through a short column (petroleum ether/CH_2Cl_2 = 1:2) to give a yellow solid (6.17 g, 46%). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 9.95 (s, 3H), 7.85 (d, 6H), 7.25 (s, 6H).

Tetrakis(4-bromophenyl)methane (8)

To a two-necked round bottom flask containing tetraphenylmethane (**TPM**) (0.9 g, 2.8 mmol) was added slowly Br_2 (2.5 ml, 98 mmol). The mixture was stirred at room temperature for 5 h. To the above mixture was added the -78 °C ethanol, filtered, washed with the solution of $Na_2S_2O_3$ in water. The crude product was purified by silica gel column chromatography (PE). Compound **8** was obtained as a white solid (1.59 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 7.39 (d, 8H) 7.01 (d, 8H).

Tetrakis(4-formylphenyl)methane (3)[S4]

To a two-necked round bottom flask containing tetra(4-bromophenyl)methane **8** (1.12 g, 1.76 mmol) was added tetrahydrofuran (150 ml) under nitrogen. n-butyllithium (6.4 ml, 16 mmol) was dropwise into the above mixture at -78 °C. N,N-dimethylformamide (2.5 ml, 32 mmol) was added after the mixture was stirred for 40 min. Then, the mixture was stirred overnight and allowed to warm to room temperature. The mixture was concentrated in vacuum, washed with dichloromethane, water and brine, the organic phase was dried over $MgSO_4$, filtered and purified by silica gel column chromatography (CH_2Cl_2) to give a colorless solid (328mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.02 (s, 4H), 7.84 (d, 8H), 7.44 (d, 8H).

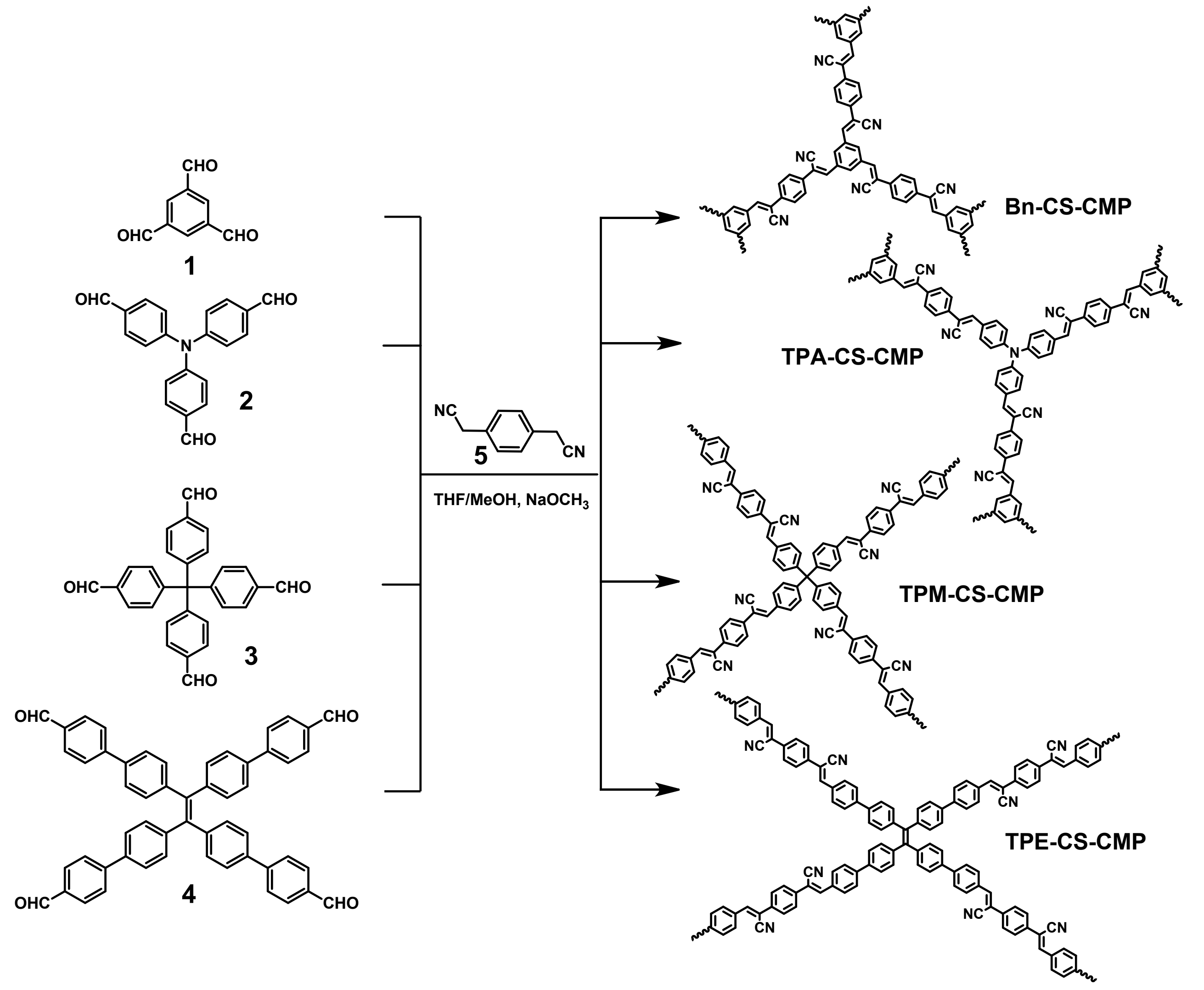
1,1,2,2-tetrakis(4-bromophenyl)ethene (9)

To a two-necked round bottom flask containing 1,1,2,2-tetraphenylethene (**TPE**) (7.7 g, 23.2 mmol) was added slowly Br_2 (11.5 ml, 461 mmol). Then the mixture was stirred at room temperature for 20 h. Br_2 was quenched with the solution of $Na_2S_2O_3$ in water and dichloromethane was added to the above mixture to dissolve the crude product. The organic layer was dried over $MgSO_4$ and concentrated in vacuum, the residue was purified by silica gel column chromatography (petroleum ether) to give a white solid (13.9 g, 93%).^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.26 (d, 8H), 6.84 (d, 8H).

4',4''',4''''',4'''''''-(ethene-1,1,2,2-tetrayl)tetrakis(([1,1'-biphenyl]-4-carbaldehyde)) (4)[S5]

To a Schlenk tube containing 1,1,2,2-tetrakis(4-bromophenyl)ethene **9** (324 mg, 0.5 mmol), 4-formylphenylboronic acid **10** (450 mg, 3 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) was added the degassed dioxane (8 ml) and the solution of

K_2CO_3 (553 mg, 4 mmol) in 2 ml water under nitrogen. The mixture was stirred at 85°C for 3 days. The mixture was cooled to room temperature and poured into cold diluted hydrochloric acid. The formed precipitate was filtered and purified by silica gel column chromatography (petroleum ether/dichloromethane = 1:1) to give a green solid (255 mg, 68%) . ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.04 (s, 4H), 7.92 (d, 8H), 7.74 (d, 8H), 7.48 (d, 8H), 7.23 (d, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 191.84, 146.37, 143.64, 140.76, 137.96, 135.24, 132.13, 130.28, 127.41, 126.87.



Scheme S2. Synthesis of **Bn-CS-CMP**, **TPA-CS-CMP**, **TPM-CS-CMP** and **TPE-CS-CMP.**

Note: For the optimization of Knoevenagel polycondensation, we screened various conditions including solvent (THF/MeOH; CH_2Cl_2/MeOH; Dioxane/EtOH; $CHCl_3$/EOH), bases (NaOH, NaOMe, KOt-Bu, Na_2CO_3, Cs_2CO_3), reaction temperatures (0°C, r.t. and 50°C), and concentration of **5** (0.1, 0.3, 0.5, 0.75, and 1 mM). By comparing different results, we finally fixed at using THF/MeOH as co-solvent, NaOMe as the base, reacted at room temperature for convenience and fix the concentration of the functional groups at 1.5 M.

Bn-CS-CMP

To a Schlenk tube containing 1,3,5-benzenetricarboxaldehyde **1** (649 mg, 4 mmol), 1,4-phenyleneacetonitrile **5** (937 mg, 6 mmol) was added THF (40 ml) under nitrogen. The solution of NaOMe (0.972 g, 18 mmol) in methanol (40 ml) was added into the above mixture. Precipitate was formed. The mixture was stirred at room temperature for 24 h. The mixture was quenched by diluted hydrochloric acid (5% HCl), filtered, washed with water, methanol, dichloromethane, dried in vacuum at 120 °C for 12 h to give a pale solid (1.288 g, 94%). Elemental analysis (wt%) calcd. For $\{C_{48}H_{24}N_6\}_n$: C 84.19, H 3.53, N 12.27; found: C 78.55, H 4.16, N 11.44.

TPA-CS-CMP

To a two-necked round bottom flask containing tri(4-formylphenyl)amine **2** (659 mg, 2 mmol), 1,4-phenyleneacetonitrile **5** (469 mg, 3 mmol) was added THF (20 ml) and the solution of NaOMe (324 mg, 6 mmol) in methanol (20 ml) under nitrogen. The mixture was stirred at room temperature for 24 h and quenched with diluted hydrochloric acid (5% HCl), filtered, washed with water, methanol, dichloromethane until the mother liquid was colorless. The obtained solid was dried in vacuum at 120 ^{o}C for 12 h to give a red solid (0.989 g, 97%). Elemental analysis (wt%) calcd. For $\{C_{72}H_{42}N_8\}_n$: C 84.85, H 4.15, N 11.00; found: C 76.71, H 4.82, N 10.74.

TPM-CS-CMP

To a two-necked round bottom flask containing tetrakis(4-formylphenyl)methane **3** (216 mg, 0.5 mmol), 1,4-phenyleneacetonitrile **5** (156 mg, 1 mmol) was added THF (5 ml) and the solution of NaOMe (108 mg, 2 mmol) in methanol (5 ml) under nitrogen. The mixture was stirred at room temperature for 24 h and quenched with diluted hydrochloric acid (5% HCl), filtered, washed with water, methanol, dichloromethane until the mother liquid was colorless. The solid was dried in vacuum at 120 ^{o}C for 12 h to give a yellow solid (0.312 g, 93%). Elemental analysis (wt%) calcd. For $\{C_{98}H_{56}N_8\}_n$: C 87.48, H 4.19, N 8.33; found: C 78.57, H 4.62, N 6.92.

TPE-CS-CMP

To a two-necked round bottom flask containing 4',4''',4''''',4'''''''-(ethene-1,1,2,2-tetrayl)tetrakis(([1,1'-biphenyl]-4-carbaldehyde)) **4** (375 mg, 0.5 mmol), 1,4-phenyleneacetonitrile **5** (156 mg, 1 mmol) was added THF (20 ml) and the solution of NaOMe (162 mg, 3 mmol) in methanol (5 ml) under nitrogen. The mixture was stirred at room temperature for 40 h and quenched with diluted hydrochloric acid (5% HCl), filtered, washed with water, methanol, dichloromethane until the mother liquid was colorless. The solid was dried in vacuum at 120 ^{o}C for 12h to give a brown solid (0.427 g, 86%). Elemental analysis (wt%) calcd. For $\{C_{148}H_{88}N_8\}_n$: C 89.85, H 4.48, N 5.66; found: C 86.30, H 4.05, N 4.79.

Section 3. FT-IR Spectroscopy

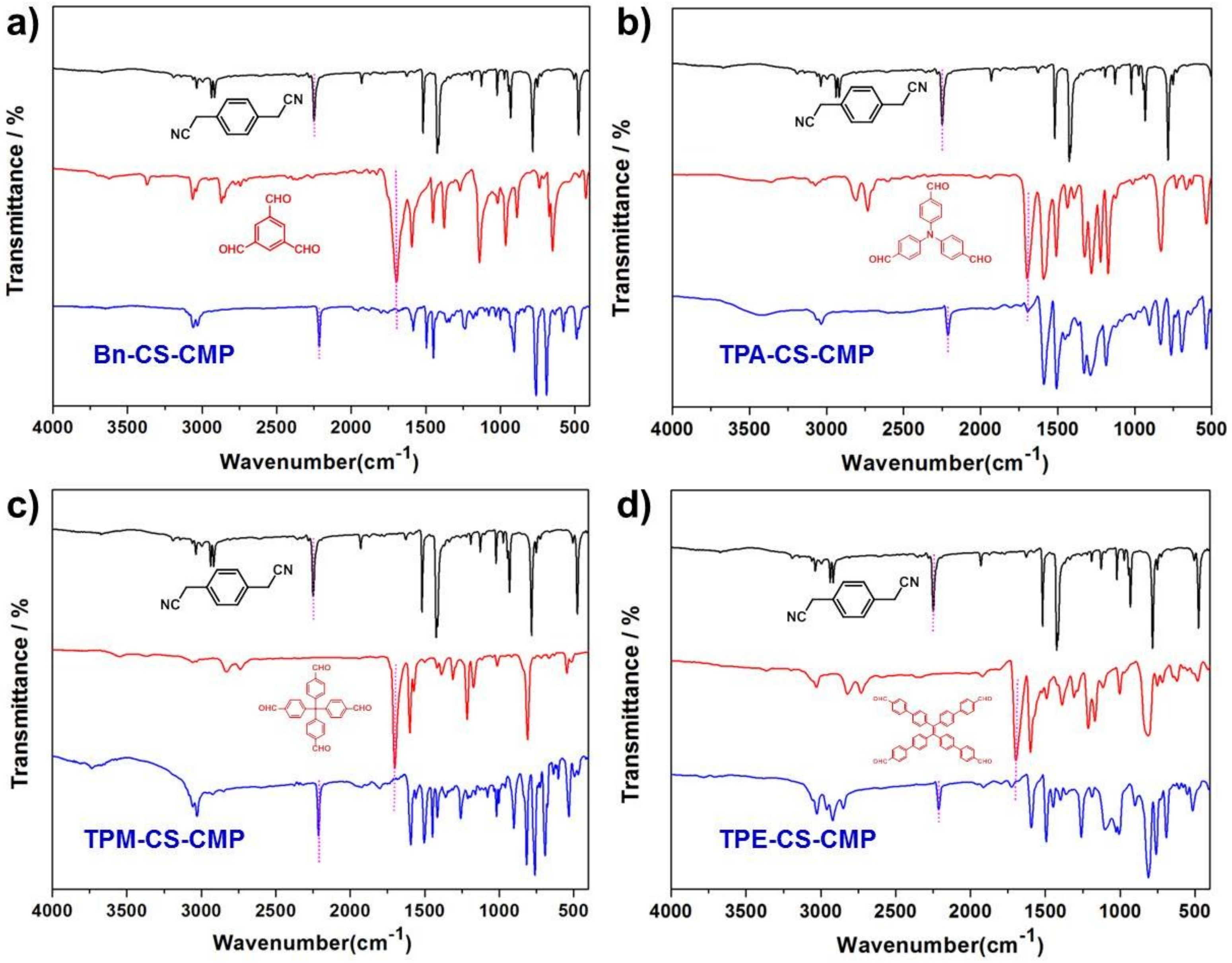


Fig. S1 FT-IR spectra of 1,4-phenyldiacetonitrile (black line), aldehydes (red line), and the **CS-CMP**s (blue line).

Section 4. Thermogravimetric Analysis

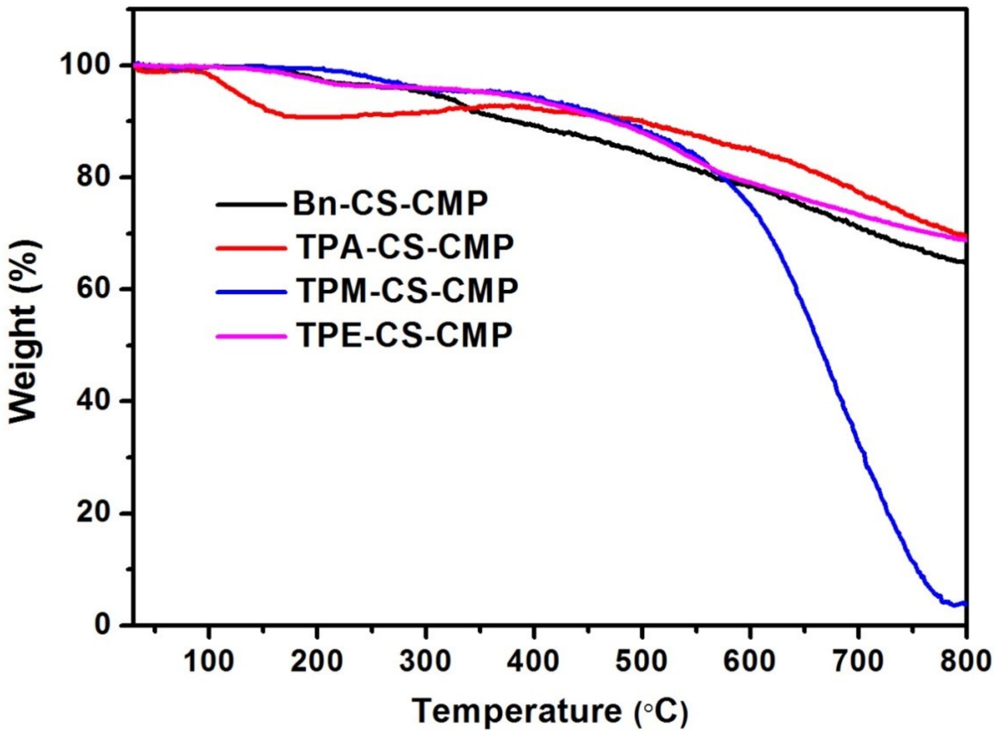


Fig. S2 The TGA curves of **Bn-CS-CMP** (black line), **TPA-CS-CMP** (red line), **TPM-CS-CMP** (blue line), **TPE-CS-CMP** (pink line).

Section 5. PXRD profiles

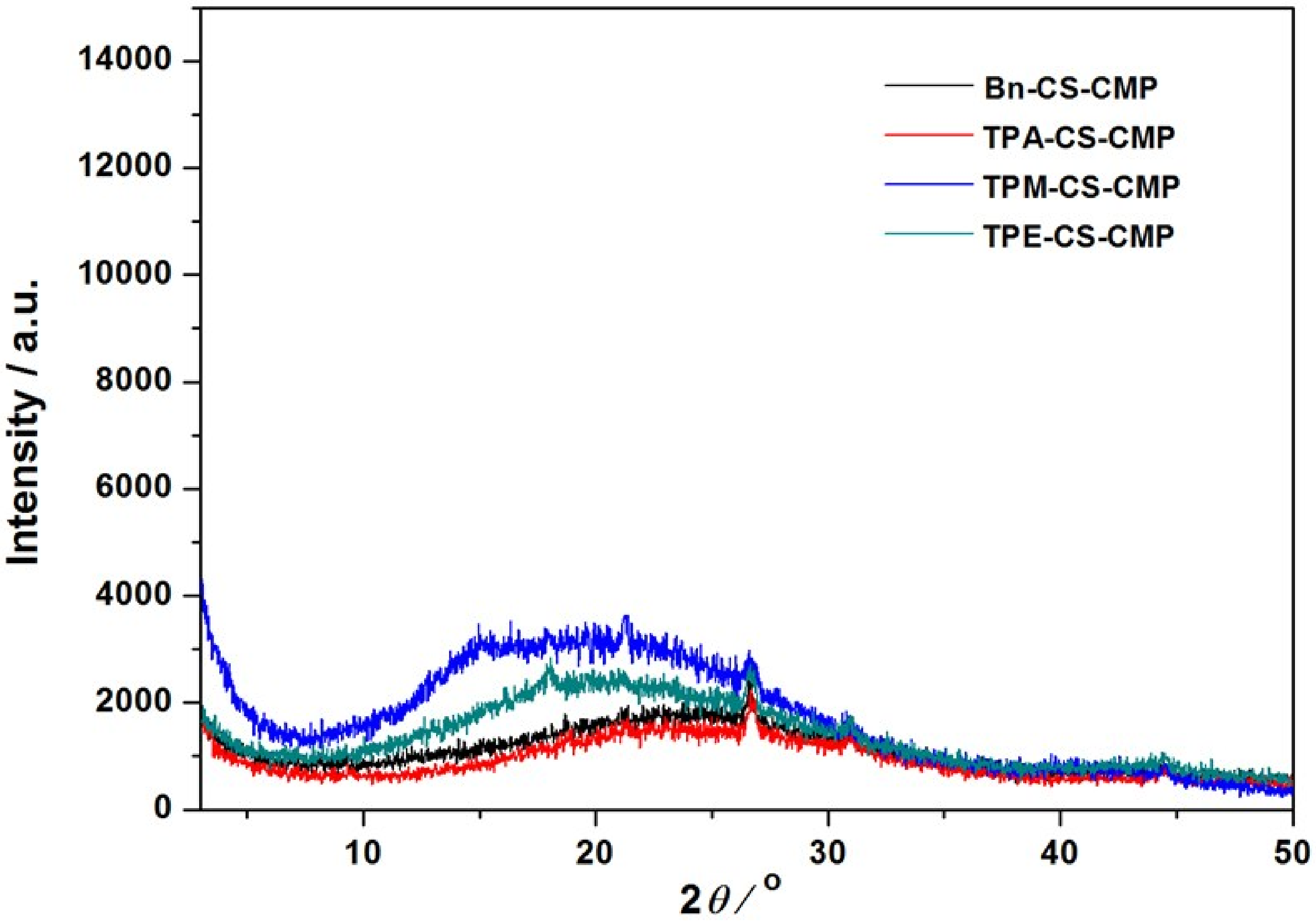


Fig. S3 Powder X-ray diffraction pattern of **Bn-CS CMP** (black line), **TPA-CS CMP** (red line), **TPM-CS CMP** (blue line), and **TPE-CS CMP** (cyan line).

Section 6. SEM & TEM images

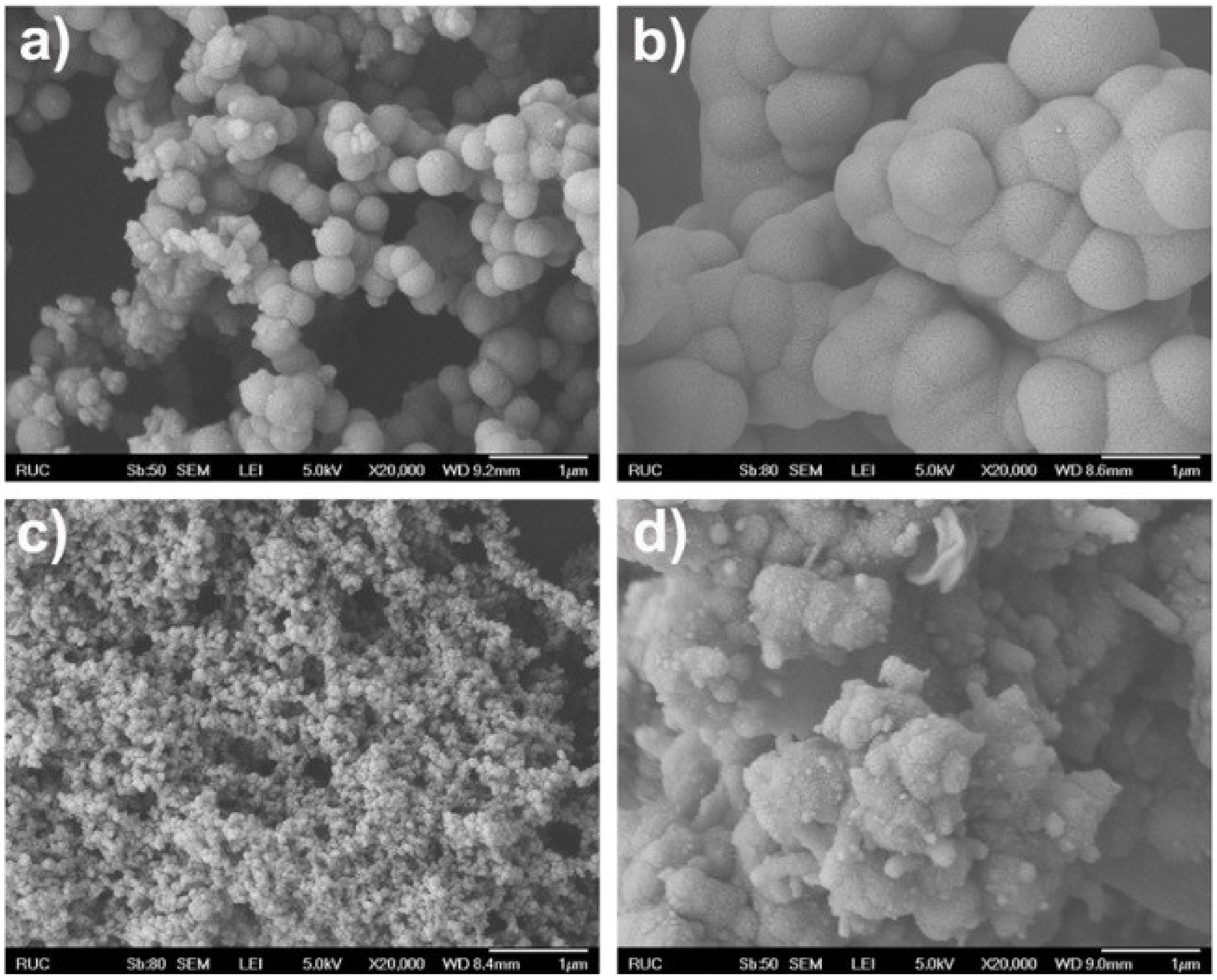


Fig. S4 SEM images of a) **Bn-CS-CMP**, b) **TPA-CS-CMP**, c) **TPM-CS-CMP** and d) **TPE-CS-CMP** (all the scale bars are 1 μm).

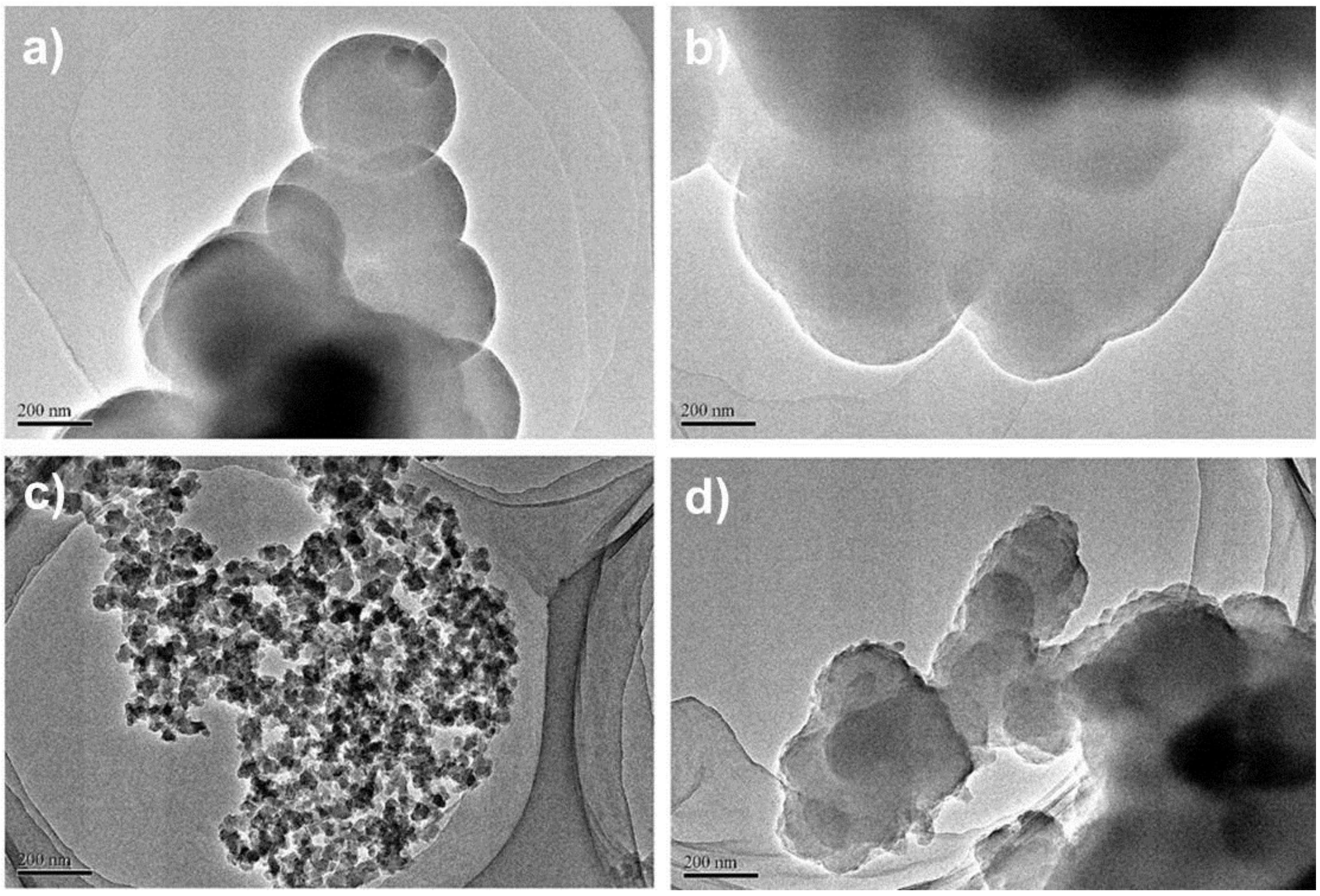


Fig. S5 TEM images of a) **Bn-CS-CMP**, b) **TPA-CS-CMP**, c) **TPM-CS-CMP** and d) **TPE-CS-CMP** (all the scale bars are 200 nm).

Section 7. Photographs of CS-CMPs's Suspension

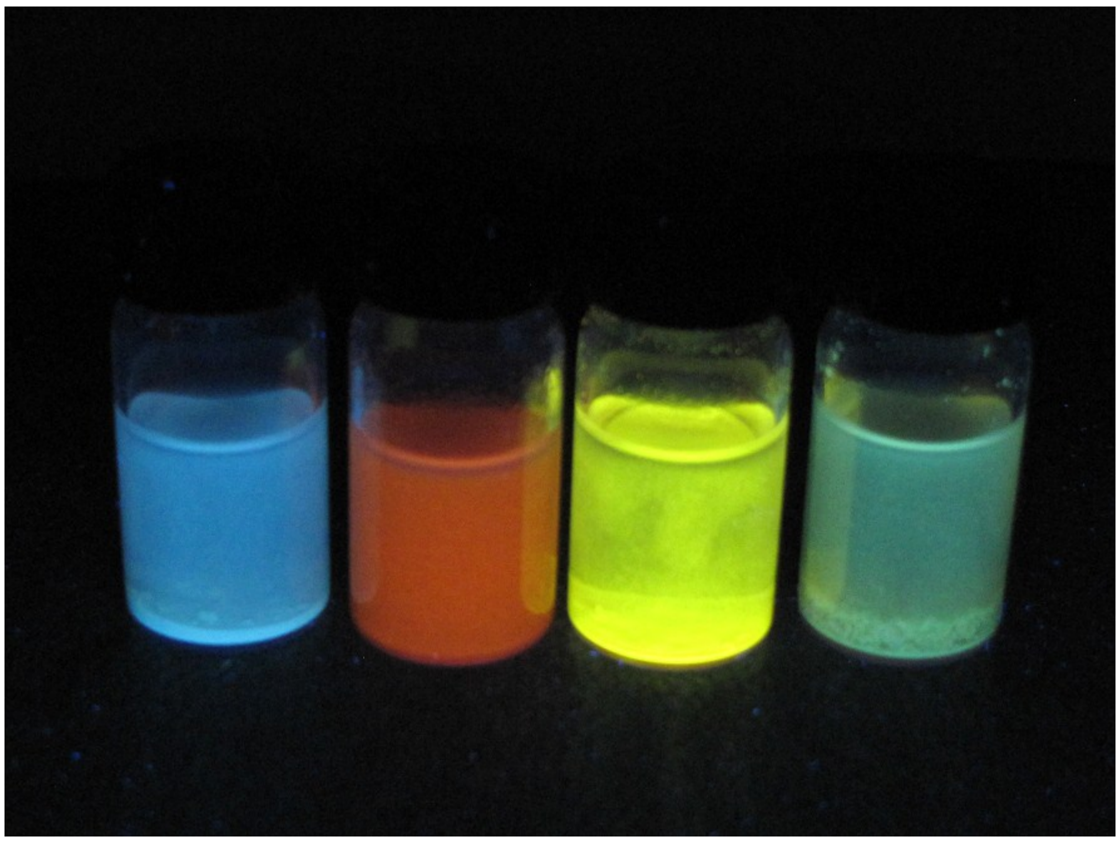


Fig. S6 The photographs of the four CS-CMPs suspended in dicholoromethane. (from left to right are: **Bn-CS-CMP**, **TPA-CS-CMP**, **TPE-CS-CMP**, and **TPM-CS-CMP**)

Section 8. CIE chromaticity diagram

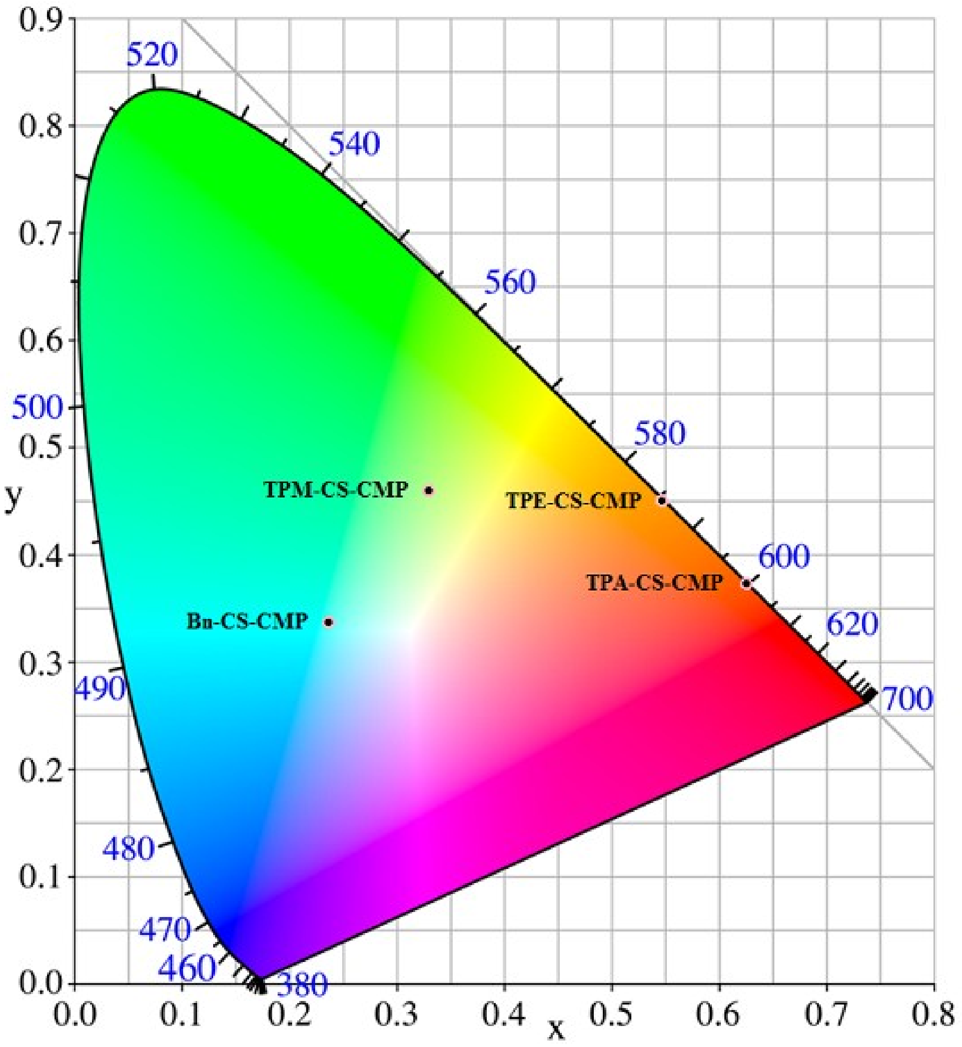


Fig. S7 The CIE coordinates of these four **CS-CMP**s (dots on the diagram): (0.24, 0.34) for **Bn-CS CMP**, (0.33, 0.46) for **TPM-CS CMP**, (0.55, 0.45) for **TPE-CS CMP**, and (0.63, 0.37) for **TPA-CS CMP**.

Section 9. Solid-state fluorescence Quantum Yield Calculation

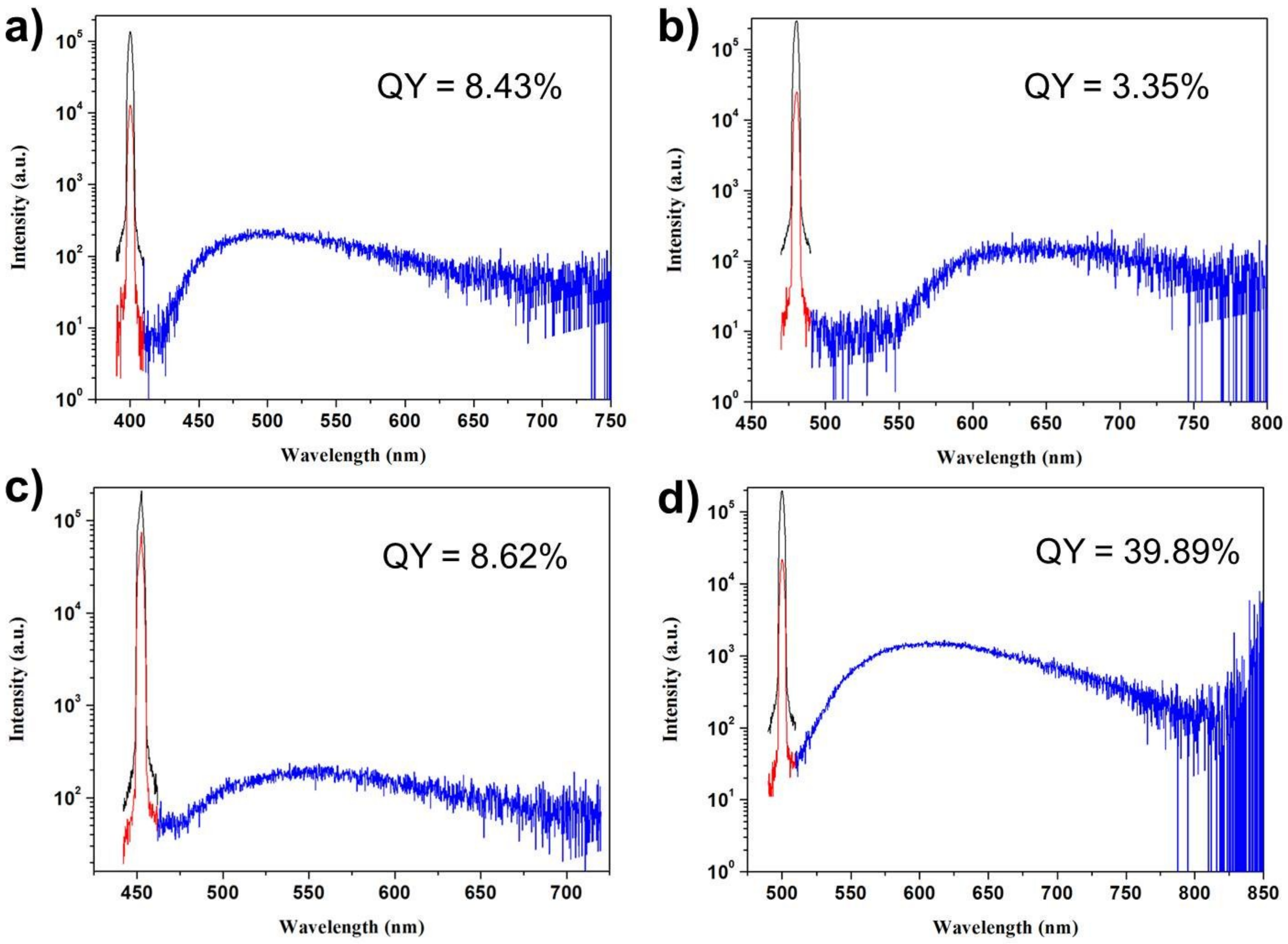


Fig. S8 The fluorescence quantum yield of a) **Bn-CS-CMP**, b) **TPA-CS-CMP**, c) **TPM-CS-CMP**, and d) **TPE-CS-CMP** measured in the solid state at room temperature. Excitation wavelength is 400, 480, 452, and 500 nm for **Bn-CS-CMP**, **TPA-CS-CMP**, **TPM-CS-**

CMP, and **TPE-CS-CMP** respectively. Black line: reflectance from Spectralon®, red line: reflectance from samples, blue line: emission spectra from the samples. The sample quantum yields was calculated by the following equation: $\Phi_x = \Phi_{st}\,(1\text{-}R_{st}I_x)/(1\text{-}R_xI_{st})$. R_x and R_{st} represent diffuse reflectance of the sample and the standard, respectively (in a particular wavelength). $\Phi_x = \Phi_{st}$ are the quantum yields of solid samples and the standard, respectively. I_x and I_{st} represent the integrated emission spectrum of the sample and the standard, respectively.

Section 10. Fluorescence decay curves

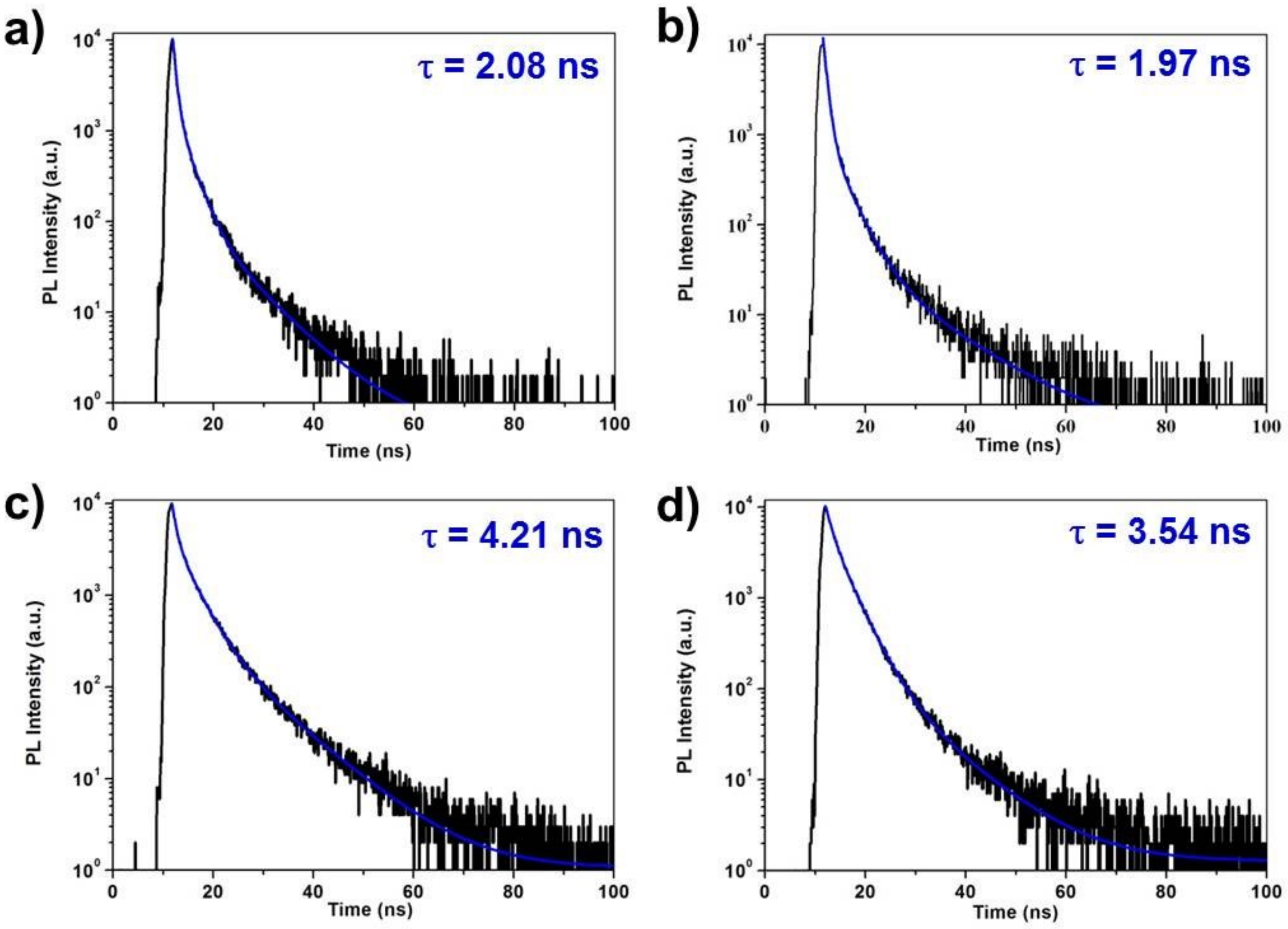


Fig. S9 Fluorescence decay curves of a) **Bn-CS-CMP**, b) **TPA-CS-CMP**, c) **TPM-CS-CMP** and d) **TPE-CS-CMP**. The decay curves were best fitted by a tri-exponential function, and thus afford the fluorescent lifetimes of **Bn-CS-CMP**, **TPA-CS-CMP**, **TPM-CS-CMP**, and **TPE-CS-CMP** to be 2.08, 1.97, 4.21, and 3.54 ns respectively.

Section 11. Supporting references

S1. B. Manna, A. K. Chaudhari, B. Joarder, A. Karmakar, S. K. Ghosh, *Angew. Chem. Int. Ed.* **2013**, *52*, 998.

S2. P. Pandey, A. P. Katsoulidis, I. Eryazici, Y. Wu, M. G. Kanatzidis, S. T. Nguyen, *Chem. Mater.*, **2010**, *22*, 4974-4979.

S3. M. I. Mangione, R. A. Spanevello, *Macromolecules*, **2013**, *46*, 4754-4763.

S4. N. Popp, T. Homburg, N. Stock, J. Senker, *J. Mater. Chem A.*, **2015**, *3*, 18492-18504.

S5. W. Luo, Y. Zhu, J. Zhang, J. He, Z. Chi, P. W. Miller, L. Chen, C-Y. Su, *Chem. Commun.*, **2014**, *50*, 11942-11945.