# **Electronic Supplementary Information**

# Nanoporous networks as effective stabilisation matrices for nanoscale zero valent iron and groundwater pollutant removal

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#### S1 - Chemicals

Acetone (99.0%), activated carbon (charcoal, powder, BET surface area: ~ 890 m<sup>2</sup>/g), dimethyl sulfoxide (99.0%), ethanol (95.0%, denatured), ferric chloride (98.0%), N-N-dimethylformamide (99.0%), melamine (99.0%), and nitric acid (60.0%) were obtained from Samchun Chemical Co. (Pyeongtaek, Gyeonggi-do, Korea). Cyanuric chloride (99.0%), dichloromethane (99.8%), 4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid (HEPES, 1M in H<sub>2</sub>O), piperazine (99.0%), 4-4'-thiobisbenzenethiol (98.0%), terephthalaldehyde (99.0%), and trimesoyl chloride (98.0%) was obtained from Sigma-Aldrich (St. Louis, MO, USA). Naphthol blue black (97.0%), N,N-diisopropylethylamine (DIPEA, 98.0%), and 1,1,1-tris(4-hydroxyphenyl)-ethane (98.0%) was obtained from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Sodium borohydride (97.0%) was obtained from Daejung Chemical & Metals Co., Ltd. (Siheung-si, Gyeonggi-do, Korea). 2,2',4,4'-tetrahydroxybenzophenone (98.0%) was obtained from Alfa Aesar (Ward Hill, MA, USA). N,N-dimethylformamide (DMF, pure, anhydrous), 1,4-dioxane (pure, anhydrous), and tetrahydrofuran (pure, anhydrous) were obtained Samchun Chemical Co. and purified using the Glass Contour Ultimate Solvent Purification System (Nikko Hansen Co., Ltd., Japan). Unless otherwise stated, all chemicals were used as received from the supplier. All solutions, unless specifically stated, were

prepared using deionized water (DIW).



#### S2 – Chemical composition of COPs and synthesis procedures of COP60 and COP61

COP60 was prepared by first mixing a solution of 1.47g (5.97 mmol) 2,2',4,4'-tetrahydroxybenzophenone and 2.62 mL DIPEA dissolved in 130 mL tetrahydrofuran. Then, adding drop-wise, a solution of 1 g (3.76 mmol) trimesoyl chloride dissolved in 20 mL tetrahydrofuran was mixed with the initial solution with aggressive stirring. The obtained precipitates were stirred for 24 hours at room temperature, filtered, and washed with tetrahydrofuran, water, and ethanol. The off-white precipitates were dried at 80°C in vacuum for 24 hours, resulting in 2.22 g of product. COP61 was prepared by first mixing a solution of 1.788g (5.84 mmol) 1,1,1-tris(4-hydroxyphenyl)-ethane and 2.62 mL DIPEA dissolved in 130 mL tetrahydrofuran. Then, adding drop-wise, a solution of 1 g (3.76 mmol) trimesoyl chloride dissolved in 20 mL tetrahydrofuran was mixed with the initial solution with aggressive stirring. The obtained precipitates were stirred for 14 hours at room temperature, filtered, and washed with aggressive stirring. The obtained precipitates were stirred for 14 hours at room temperature, filtered, and washed with tetrahydrofuran, water, and ethanol. The off-white precipitates were stirred for 14 hours at room temperature, filtered, and washed with tetrahydrofuran, water, and ethanol. The off-white precipitates were stirred for 14 hours at room temperature, filtered, and washed with tetrahydrofuran, water, and ethanol. The off-white precipitates were dried at 80°C in vacuum for 24 hours, resulting in 2.28 g of product.

#### S3 – Fourier transform infrared spectroscopy (FTIR)

COP1 exhibited FTIR peaks around 2940 cm<sup>-1</sup> indicating the absorption bands of saturated carbons of piperazine, and COPs 1 and 6 exhibited peaks at 1600 - 1200 cm<sup>-1</sup> indicating typical stretching of CN heterocycles, 800 cm<sup>-1</sup> indicating the typical breathing mode of triazine, while showing the absence of a peak at 850 cm<sup>-1</sup> indicating the elimination substitution of C-Cl bonds. COP19 exhibited FTIR peaks at 3420 and 1550 cm<sup>-1</sup> indicating primary amine groups for NH<sub>2</sub> stretching and deformation respectively, 2970 cm<sup>-1</sup> indicating C-H stretching, 1690 cm<sup>-1</sup> indicating C=O stretching, and the absence of a peak at 1600 cm<sup>-1</sup> indicating the lack of imine linkages and C=N stretching. COPs 60 and 61 exhibited wide peak area in the range of 4000 – 2500 cm<sup>-1</sup> indicating the presence of multiple hydroxyl groups, a peak at 1756 cm<sup>-1</sup> indicating the C=O bond, and a lack of a peak at 1035 cm<sup>-1</sup> indicating the elimination substitution of C-Cl bonds.



Figure S1: FTIR spectrum of COP1 via KBr pellet.



Figure S3: FTIR spectrum of COP19 via KBr pellet.



Figure S5: FTIR spectrum of COP61 via KBr pellet.



Figure S6: XRD scan of the COP6 composite over a period of  $5 - 80^{\circ} 2\theta$ .



Figure S7: XRD scan of the COP60 composite over a period of  $5 - 80^{\circ} 2\theta$ .



Figure S8: XRD scan of the COP61 composite over a period of  $5 - 80^{\circ} 2\theta$ .



Figure S9: XRD scan of pure nZVI over a period of  $5 - 80^{\circ} 2\theta$ .

### S5 – Dye decolorization spectra via UV-Vis spectroscopy



Figure S10: Naphthol blue black decolorization absorbance spectra via COP6 composite using UV-Vis spectroscopy.



Figure S11: Naphthol blue black decolorization absorbance spectra via COP60 composite using UV-Vis spectroscopy.



Figure S12: Naphthol blue black decolorization absorbance spectra via COP61 composite using UV-Vis spectroscopy.



S6 - N<sub>2</sub> adsorption-desorption isotherms

Figure S13:  $N_2$  adsorption-desorption isotherms of bare COP polymers and their composites measured at 77 K; (A) COP-1, (B) COP-6, (C) COP-19, (D) COP-60, and (E) COP-61. (E) Corresponding Barrett-Joyner-Halenda (BJH) average pore size of bare COPs and the composites.

## S6 – Dye decolourization comparison – polymers vs. composites



Figure S14: Dye decolourization of both the bare polymers (A) and the composites (B).