

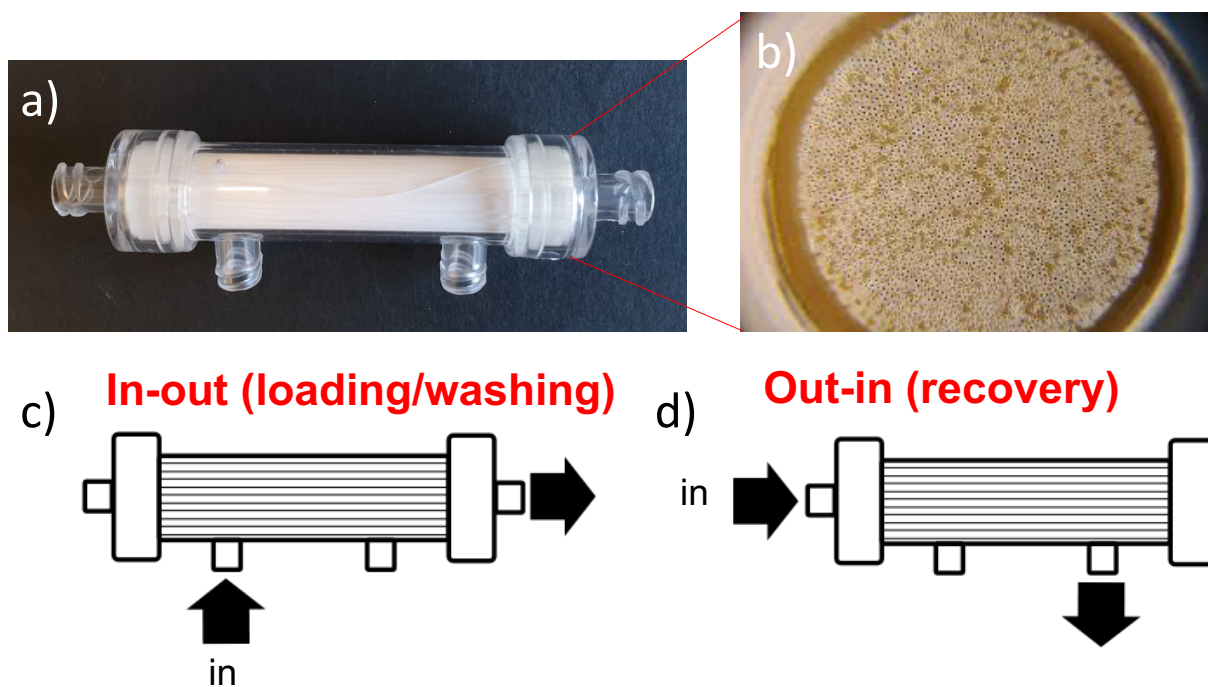
## **Electronic Supplementary Material for:**

### **Scalable synthesis and purification of functionalized graphene nanosheets for water remediation**

#### **Contents:**

1. Microfiltration module structure
2. Synthesis
3. PEI loading estimation
4. Thermal Gravimetric Analysis (TGA)
5. Attenuated Total Reflection–Fourier Transform Infra-Red (ATR-FTIR) spectroscopy
6. X-Ray Photoelectron spectroscopy (XPS)
7. X-Ray Diffraction (XRD)
8. Contact angle measurements

## 1. Microfiltration module structure



**Figure S1.** Dead-end Microfiltration and recovery procedures. a) image of a PES cartridge (Plasmart 25 model, 11 mm length,  $\Phi_{\text{int}}=60$  mm), about 275 hollow fibers, 700 mg weight ( $\Phi_{\text{int}}=50$   $\mu\text{m}$ ,  $\Phi_{\text{ext}}=300$   $\mu\text{m}$ , cut-off= 0.1-0.2  $\mu\text{m}$ ), b) zoom of the edge of the cartridge with the epoxy resin closing the interspace between the fibers, c) sketch of the in-out filtration mode used to load the reaction crude and to wash it and d) sketch of the out-in filtration mode used to recover the GOPEI.

The models used for microfiltration were: Plasmart 25, SF 0.01m<sup>2</sup> (about 275 fibers), cut off 1000Kda, pore size 100-200 nm, dead volume 2,5 ml, maximum graphene loading (Abalonyx AS, Norway, powder sonicated for 4 hours) estimated about 500 mg.

Plasmart 100, SF 0.1 m<sup>2</sup>, (about 850 fibers), cut off 1000Kda, pore size 100-200 nm, dead volume 15 mL, maximum graphene loading (Abalonyx, powder sonicated for 4 hours) estimated about 1.5 gr

The choice was dictated by the reaction scale. For amount of initial GO lower than 1 g we used the Plasmart 25 model.

## 2. Synthesis

**General.** Branched PEI (average Mw ~25,000 Da by LS, average Mn ~10,000); ethanol, 96% (EtOH); dichloromethane (DCM) were purchased from Sigma Aldrich and used without further purification. GO powder was purchased from Abalonyx AS, Norway.

Microwave assisted reactions were performed by a CEM Matthews, NC (USA) DISCOVER-SP (Freq. 2,45 GHz; Max Pwr. 1100 W).

Absorbance spectra were obtained with Carry 3500 UV-vis spectrophotometer (Agilent Technologies, Australia). Photoluminescence spectra were obtained with a LS50 spectrofluorometer (PerkinElmer, Waltham, MA, USA).

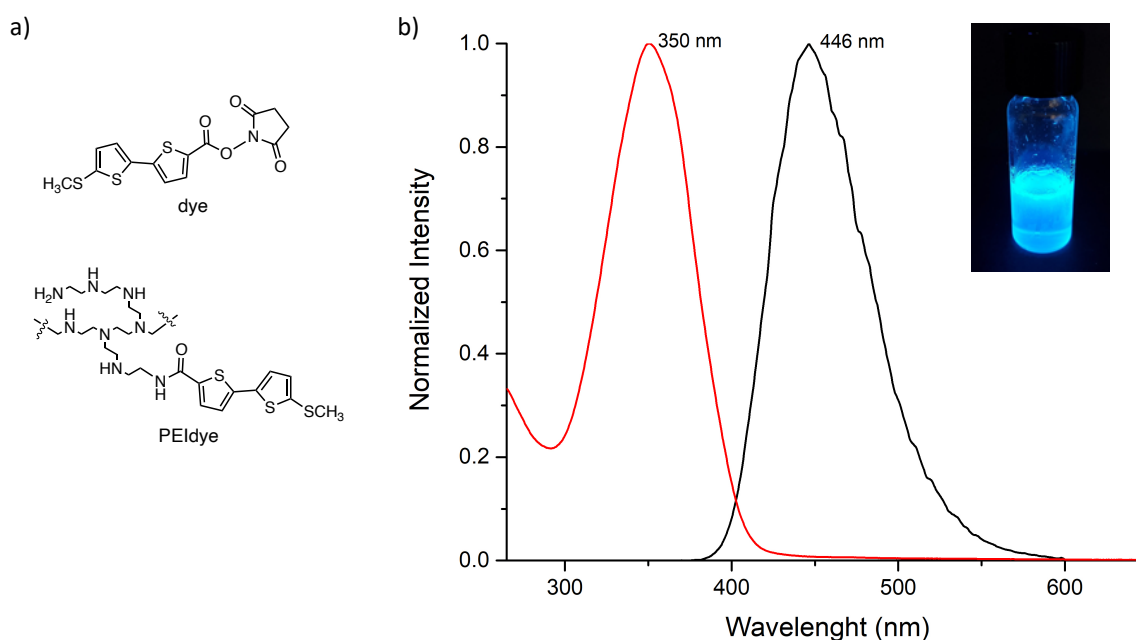
## 2.1 Synthesis of PEI-dye:

The thiophene dye (2,5-dioxopyrrolidin-1-yl 5'-(methylthio)-[2,2'-bithiophene]-5-carboxylate, <sup>1</sup> 5 mg, Mw=353) was dissolved in 5 mL of DCM and added to 100 mg of PEI dissolved in 20 mL DCM at room temperature.

The mixture was stirred overnight, the solvent evaporated under vacuum and the product was used without further purification.

**2.2 Synthesis of GOPEI dye:** GO (Abalonyx, suspension 4 mg/mL, 25 mL) was dispersed in 25 mL of EtOH and the resulting mixture was sonicated for 30 min; then the PEI dye, previously synthesized, dissolved in 25 mL EtOH was added to the suspension and the mixture was irradiated with MW as for the synthesis of GOPEI and the crude purified by microfiltration (110 mg recovered).

Figure S4 shows the evolution of the absorbance decay in fractions eluted by the microfiltration of GOPEI dye as well as the fluorescence intensity decrease of the same fractions under UV-vis illumination. The comparison of the absorption intensity with a calibration curve of PEI dye absorption allow us to estimate a PEI loading of about 36%, in good accordance with that estimated by Cu-binding experiments and weighting of evaporated recovered PEI fractions, as described above.



**Figure S2.** a) molecular structure of the thiophene dye and PEI dye, b) UV-vis and PL emission spectra of the PEI dye in CH<sub>2</sub>Cl<sub>2</sub> (0,2 mg/ml) and image of the solution under illumination at 365 nm.

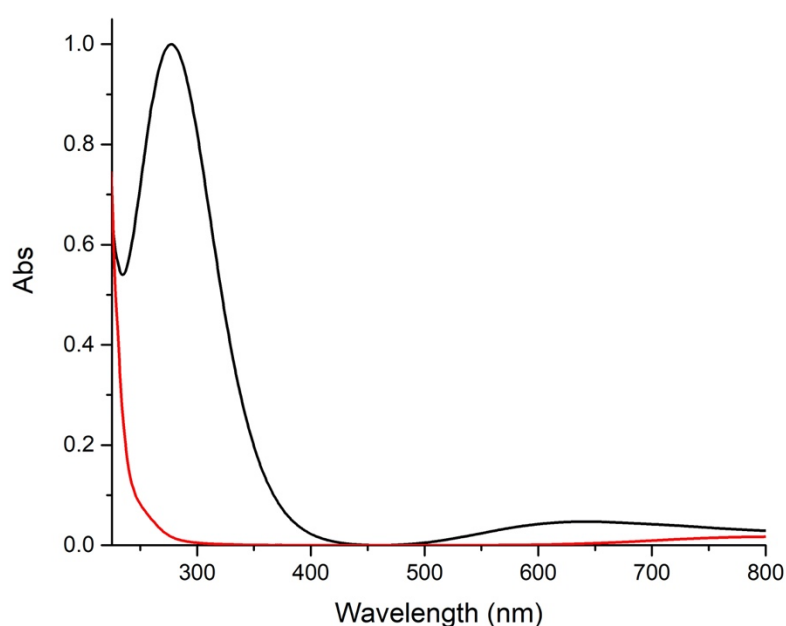
## 3. PEI loading estimation

The monitoring of PEI amount in the washing water fractions was performed by UV-vis spectroscopy after complexation with copper salts (fig. S3). Briefly, a solution of copper salt was prepared dissolving 100 mg of CuCl<sub>2</sub> in 100 mL of DI water. In parallel, a solution of PEI was prepared dissolving 20 mg of PEI in 100 mL DI water and mixed to copper solution at different ratio in order to obtain five standard solution of Cu-PEI complex and to create the calibration curve. To evaluate the amount of unreacted PEI in each fraction, 0.5 mL of eluted sample was mixed with 0.5 mL of a solution of CuCl<sub>2</sub> (concentration 1.0 mg/mL) and 2.0 mL of DI water, then the adsorption spectrum was collected.

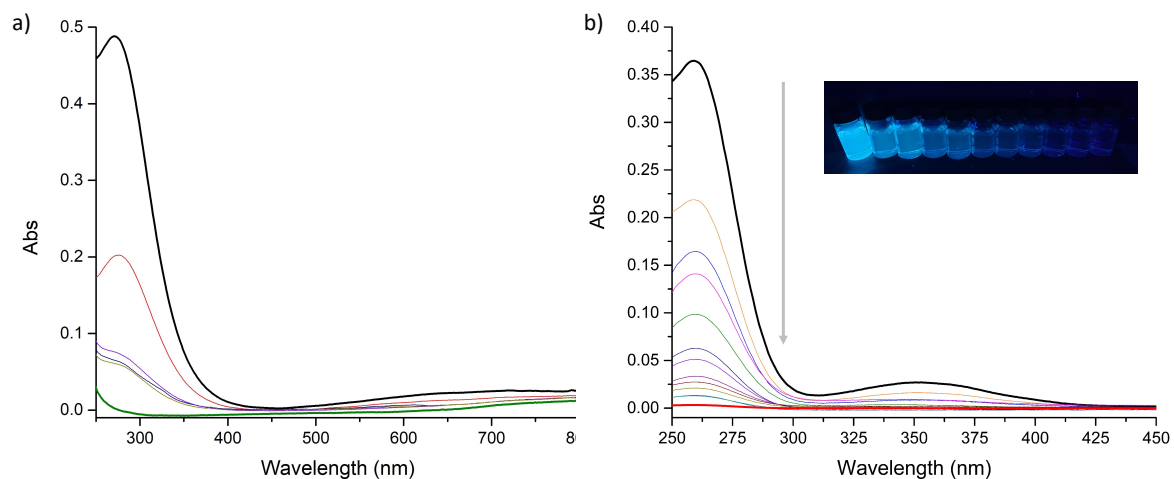
<sup>1</sup> M. Zambianchi, A. Barbieri, A. Ventola, L. Favaretto, C. Bettini, M. Galeotti, G. Barbarella *Bioconjugate Chem.*, Vol. 18, No. 3, 2007, 1004–1009

Washing with water-ethanol of immobilized GOPEI was carried out until no (absorbance) peak at 277 nm (ascribed to PEI-Cu complex, fig. S4a) was observed. Then by collecting the eluted fraction, complexing them as described above, and using a calibration curve ( $R^2= 0,99985$ ) it was possible to estimate a PEI loading of about 40%. This value was confirmed also by weighting the evaporated recovered PEI fractions.

In parallel, we also estimate the evolution of the purification and the PEI loading by monitoring the evolution of the fluorescence intensity which decrease of the eluted fractions during the microfiltration under UV-vis illumination as well as the absorbance decay of the same fractions (fig. S4b). The comparison of the absorption intensity with a calibration curve of PEIdye absorption allow us to estimate a PEI loading of about 37%, in good accordance with that estimated by Cu-binding experiments. A total volume of water required for complete removal of PEIdye of about 2.8L/gram of GOPEIdye (crude of reaction).

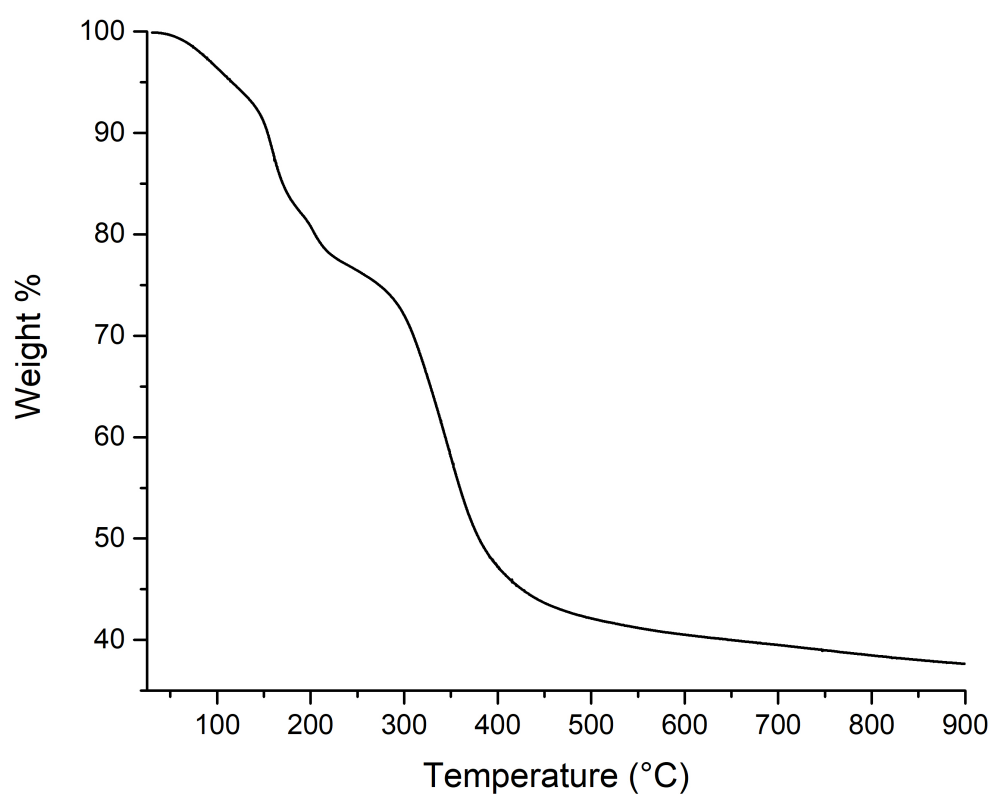


**Figure S3.** Absorbance spectra of Cu-PEI (black line) and CuCl<sub>2</sub> (red line).



**Figure S4.** a) UV-vis absorption spectra of eluted fractions upon Cu complexation. b) UV-vis absorption spectra of the eluted fractions. (Black line: first fraction; Red line: last fraction).

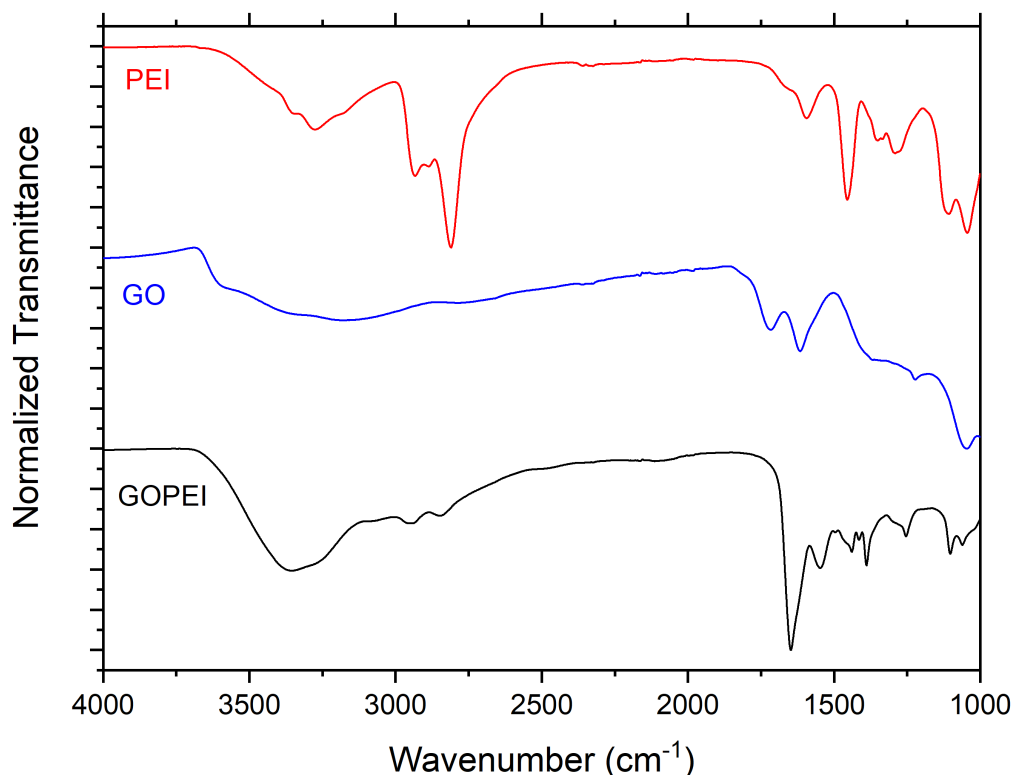
#### 4. Thermal Gravimetric Analysis (TGA)



**Figure S5.** TGA profile of GOPEI.

GOPEI profile displays a weight loss of ca. 20% in the range of 150–300 C caused by decomposition of oxygen functional groups of GO.<sup>2</sup> The weight loss of about 35% in the range 250°C-350°C is typical of PEI thermal degradation.<sup>3</sup> This value is in good accordance with the PEI loading estimated by microfiltration post experiments and XPS data.

## 5. Attenuated Total Reflection–Fourier Transform Infra-Red (ATR-FTIR) spectroscopy



**Figure S6.** ATR-FTIR spectra of GO, PEI and GOPEI. Spectra were collected by Agilent Cary 630 FTIR.

## 6. X-Ray Photoelectron spectroscopy (XPS)

High-resolution XPS spectra were acquired by using a Phoibos 100 hemispherical energy analyser (Specs GmbH, Berlin, Germany), equipped with Mg Ka radiation source ( $h\nu$  1253.6 eV; power = 125W). Analyser were set in the Constant Analyser Energy (CAE) mode, with pass energy of 40 eV. An overall resolution of 1.5 eV was measured and the analyser was calibrated by the Ag 3d 5/2 (368.3 eV) and Au 4f 7/2 (84.0 eV) signals from freshly Ar<sup>+</sup> sputtered samples. Charging effects were corrected by calibration of Binding Energy on C 1s

<sup>2</sup> M. Melucci, E. Treossi, L. Ortolani, G. Giambastiani, V. Morandi, P. Klar, C. Casiraghi, P. Samori, V. Palermo *J. Mater. Chem.*, 2010, 20, 9052–9060

<sup>3</sup> A. D. Pakulski, W. Czepa, S. Witomska, A. Aliprandi, P. Pawlu, V. Patroniak, A. Ciesielski and P. Samori, *J. Mater. Chem. A* 2018, 6, 9384–9390.

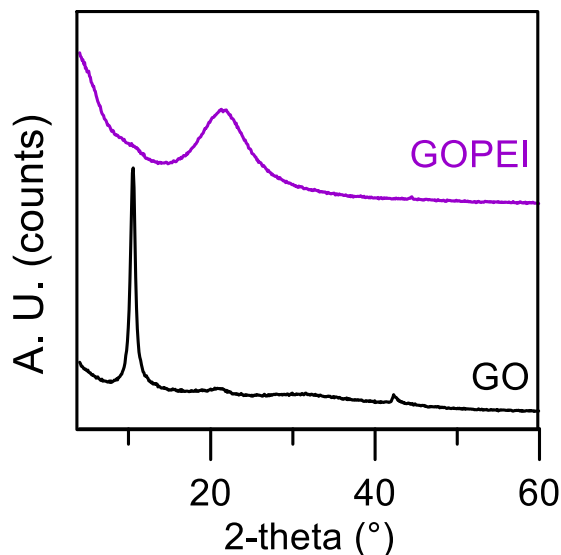
(285.0 eV) for all spectra. Unfortunately, the analysis of C 1s signal for GOPEI could not be performed since the number of synthetic components (C-C, C=C, C-OH, C-O-C, C=O, O-C=O, C-N, C-S, C(O)-N, etc..) would had been too high for a reliable fit.

XPS samples were prepared by fixing the tablets prepared from the dry powders of each material on the sample, holed by conductive carbon tape. Base pressure in the analysis chamber during analysis was maintained at 10<sup>-9</sup> mbar. Data analysis and fitting were performed with CasaXPS software, after Shirley background subtraction.

	C 1s	O 1s	N 1s	S 2p S-O	Si 2p Si-O	Cl 2p
<b>Binding Energy (eV)</b>	<b>285.0</b>	<b>531</b>	<b>401</b>	<b>168</b>	<b>101</b>	<b>196.9</b>
<b>GO</b>	69.1±0.9	27.8±0.6	0.9±0.1	1.2±0.1	0.3±0.1	0.8±0.1
<b>GO-PEI</b>	71.2±0.9	13.4±0.4	10.4±0.5	0.4±0.1	3.1±0.3	1.5±0.2

**Table S1.** Binding energy and atomic percentage of GO, and GOPEI.

## 7. X-Ray Diffraction (XRD)



**Figure S7.** XRD profiles of GO and GOPEI powders.

## 8. Contact angle measurements



**Figure S8.** Top: membranes of GOPEI (left) and GO (right). Bottom: images of the water droplet on GO/GOPEI. GOPEI  $\theta=30.9^\circ$ , GO  $\theta=38.5^\circ$ .

Contact angle measurements were performed by using a Data Physics OCA series 25 on GO and GOPEI planar membranes.

GO membrane preparation: 10 mL of 2 mg/mL GO (Abalonyx) suspension in deionized water were sonicated for 2 hours, then filtered for 3 hours under vacuum through a PES round filter (cut from a GVS PES sheet, diameter 55 mm), mounted on a glass filter holder.

GO membrane preparation: 10 mL of 3 mg/mL GO-PEI suspension in mQ water was sonicated for 4 hours, then filtered for 3 days under vacuum through a PES round filter (cut from a GVS PES sheet, diameter 55 mm), mounted on a glass filter holder.