**Electronic Supplementary Information (ESI)**

**Fluorescence detection and removal of copper from water using a biobased and biodegradable 2D soft material**

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General Methods

All chemical reagents including graphene dioxide (GO) and solvents were analytical grade and purchased from commercial suppliers. $^1$H NMR and $^{13}$C NMR spectra were recorded on the Bruker AV-400 spectrometer with chemical shifts reported in ppm (in CDCl$_3$, TMS as internal standard) at room temperature. Electric conductivity titration was recorded on a Shengci DDS-ⅡA conductivity meter (Shanghai). Contact angle experiments were operated on a Dataphysics OCA20. Brunauer-Emmett-Teller (BET) spectra were measured on a Quantachrome autosorb IQ. SEM spectra were recorded using a JEOL JSM-7500F. Fluorescence measurements were performed on a Lengguang Luminescence spectrophotometer F97PRO (Shanghai), utilising sterna silica (quartz) cuvettes with 10 mm path length and four sides polished. Filtration experiments were performed on a 2 cm diameter Buchner funnel with a Changcheng recycled water vacuum pump SHB-III (Zhengzhou). The metals uptake was analysed using atomic absorption spectrophotometer and atomic fluorescence spectrometry. Spectral-grade solvents were used for measurements of fluoride absorption and fluorescence detection.

Synthesis of the fluorescent probe 1

Fluorescent probe 1 was synthesised following the previously published method,$^{S1}$ and was fully characterized by $^1$H NMR and $^{13}$C NMR (Fig. S6).
6-Bromo-2-(2-hydroxyethyl)benzo[de]isoquinoline-1,3-dione 4 g (12.5 mmol) and methyl piperazine 1.88 g (18.8 mmol) in 20 mL methoxyethanol were vigorously stirred and heated to reflux for 3 h. The mixture was allowed to stand overnight at room temperature. The yellow solid obtained was filtered. 3.2 g (yield 75%) pure crystals were obtained by recrystallization from aqueous ethanol.

2-(2-Hydroxyethyl)-6-(4-methylpiperazin-1-yl)benzo[de]isoquinoline-1,3-dione (3.0 g, 8.84 mmol) was dissolved in dichloromethane (100 mL), methacryloyl chloride (1.86 g, 17.68 mmol) and TEA (3.0 mL, 21.59 mmol) were added. The mixture was stirred at room temperature for 12 h, poured into 300 mL of water, the organic layer was separated and the water layer was extracted with 50 mL of dichloromethane. The combined dichloromethane extracts were washed with water and dried with anhydrous magnesium sulfate. The solvent was removed under vacuum, and 3.0 g yellow residue of probe 1 was obtained with a yield of 82%. Recrystallization twice from ethanol afforded yellow crystals.

**Preparation for NGC membrane**

TEMPO oxidised cellulose was prepared by the established literature procedure. Cotton linter (20 g) was first added to aqueous solution of sodium hydroxide (500 mL, 15%, w/v) at 60°C. The resulting mixture was stirred for 2 h, washed thoroughly with deionized water and neutralized with HCl. The mixture of this pretreated cellulose (5 g), TEMPO (0.08 g), NaBr (0.5 g) and Na₂CO₃/NaHCO₃ buffer (pH=10.8) were stirred with magnetic stirring at 600 rpm, then aqueous solution of sodium hydroxide (0.5 mol/L) was added to keep the pH at 10-11. Then ethanol was added to keep the pH constant. The resulting mixture was centrifuged (10000 r/min, 20 min), washed with deionized water and ethanol. The precipitate was dried in vacuum oven (40°C) for 24 h, then we got TEMPO oxidized cellulose (TOC).

Pre-treated cellulose (2 g) and TEMPO oxidised cellulose (2 g) were dissolved in NaOH/urea solution at -4°C. The mixture were coated on the bottom of one plate and precipitated in ethanol. Then the precipitated membrane was immersed in GO
suspension (1mg/mL) for 24h and in probe 1 solution (10^{-5} mol/L) for 24h successively to complete the NGC membrane fabrication.

**Reference**


**Fluorescence detection by NGC membrane**

We cut 2 cm × 1cm of the membrane and pasted it onto a quartz glass slide. We then placed the slide into a cuvette and added 2 mL of solvent. The copper ion solutions were then added sequentially in order to investigated the fluorescence behaviour.

**Removal of copper using NGC membrane**

For the metal uptake experiments, copper sulfate pentahydrate was used in this study. Buchner funnel with diameter 40 mm was employed as the filtration system. The amount of residual copper ions in the solution was traced by Shimadzu AA-680 atomic absorption spectrophotometer.

**Recyclability**

The recyclability of NGC membrane was recorded with 50 mg L^{-1} Cu^{2+}. The regeneration of the NGC membrane adsorbed by Cu^{2+} was performed by filtrating 100 mL of 1.0 mol L^{-1} HNO_3 solution under and 200 mL DI water. The generated NGC membrane was used for another adsorption in the subsequent cycles.
2. Characterization of GO

Figure S1. a) Raman spectroscopy of GO; b) transmission electron microscope (TEM) image of graphene oxide; c) high resolution transmission electron microscope (HRTEM) image of graphene oxide; d) selected area electron diffraction (SAED) of graphene oxide
3. Contact angle

Figure S2. The contact angle of cellulose membrane and GO-cellulose membrane.
4. Brunauer-Emmett-Teller (BET)

**Figure S3.** $\text{N}_2$ adsorption-desorption isotherms of (a) cellulose membrane and (b) GO-cellulose membrane.
5. Theoretical calculations

In order to determine how our compound can interact with GO through \(\pi-\pi\) D-A interactions, we adopted the Hunter and Sander (HS) model and carried out the calculations of electrostatic surface potentials using optimised structure of probe 1 and GO. The optimisation was carried out using MMFF94 Force Field in Avogadro. \(\pi-\pi\) D-A interactions are a face centred \(\pi\)-stacking interaction between an electron rich aromatic molecule which acts as a ‘donor’ and an electron deficient aromatic compound that acts as an ‘acceptor’. These are a subset of aromatic interactions, which differs from electron neutral or rich aromatic stacking which is usually edge to face or in an offset conformation. The HS model best explains aromatic interaction chemistry and successfully predicts the relative magnitude and geometry of aromatic interactions in solution. In HS model, the substituents on an aromatic system either will influence the quadrupolar moment of the aromatic moiety by inducing either a partial negative or positive charge.\(^\text{S3}\) This difference in quadrupolar moment then determines the geometry of the interaction whether it be face-centred stacking, offset or T-shaped.

![Figure S4](image-url) \(\pi\)-Stacking confirmations L to R face centered, offset, T-shaped and edge to face

Face-centred stacking is observed when the quadrupole moments are opposite to each other. In electron neutral aromatics such as benzene, the electron density creates a quadrupole moment where the density is concentrated above and below and plane formed by the sigma bonds. In case of electron neutral or rich aromatics the \(\pi-\pi\) interaction leads to T-Shaped or edge to face geometries as these minimize the unfavourable \(\pi-\pi\) overlap and allows interaction between the partially positive ring and an adjacent \(\pi\) cloud. In an electron deficient aromatic, the quadrupole moment is inverse meaning electron density is not concentrated above and below the ring. In these examples offset confirmations are observed due to allow overlap of the electron poor ring and electron rich periphery. Taking into account these effects, we proposed different \(\pi-\pi\) stacking arrangements, Figure S5. The optimisation of the structures was carried out using MMFF94 Force Field in Avogadro (v 1.2.0). The electrostatic surface potentials were calculated in MarvinSpace (v 16.9.5.0)
**Figure S5** Top: Optimised structure of probe 1 and GO. The optimisation was carried out using MMFF94 Force Field in Avogadro. Middle: Calculated electrostatic surface potential (red notes areas of relatively high electron density, blue denotes electron deficient areas). Bottom: proposed stacking arrangements.

6. Determination of COOH content

Figure S6. Electric conductivity titration ([NaOH] = 0.15 mol/L, V_{NaOH, equilibrium} = 2.1 mL, m_{TOC} = 0.3 g). The COOH was calculated to be 1.05 mmol/g.
7. SEM

Figure S7. SEM images of a) cellulose membrane; b) GO-cellulose membrane; c) NGC membrane; d) Cu(II)-filtrated NGC membrane.
8. $^1$H NMR and $^{13}$C NMR spectra of the fluorescent probe

**Figure S8.** $^1$H NMR and $^{13}$C NMR spectra of the fluorescent probe
9. Fluorescent spectra of membrane

**Figure S9.** Fluorescent spectra of membrane a) without and b) with GO in the solution (ethanol: water=95:5), \( \lambda_{ex} = 410 \text{ nm}, [\text{Cu}^{2+}] = 0-100 \text{ ppm}; \) c) response of fluorescence signals to \( \text{Cu}^{2+} \) concentrations by NGC membrane, a linear regression curve was then fitted to these fluorescent intensity data. The Standard Deviation was obtained by fluorescence responses to be \( \sigma = 4.7815 \), therefore, the detection limit was calculated by the formula \((3\sigma/k)\) and gave a result as \( 7.3 \times 10^{-7} \text{ M} \).
10. Fluorescence spectra of Probe 1

**Figure S10.** Fluorescence spectra of probe 1 (1x10^{-5} M) in ethanol: water (95:5 v/v), λ_{ex}=410 nm, [Cu^{2+}] = 0-0.01M.
11. The recyclability of NGC membrane

Figure S11. Metal uptake of copper ions by NGC membrane at different regeneration cycles, [Cu^{2+}] = 50 mg L^{-1}.