



A three dimensional calix[4]tube-derived covalent polymer for dye adsorption and CO₂ capture

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ABSTRACT

The three-dimensional covalent polymer **7**, based on dimeric calix[4]tube macrocycles and 1,4-diethynylbenzene bridges, was synthesized through Sonogashira coupling and investigated as a multifunctional adsorbent for water and gas remediation. This work represents, to the best of our knowledge, the first use of calix[4]tubes as building blocks for porous adsorbents, expanding the family of macrocycle-based covalent materials. The polymer forms a thermally stable, mesoporous aromatic network with a near-neutral surface ($\zeta = -0.18 \pm 3.52$ mV), enabling efficient adsorption of cationic, anionic, neutral, and zwitterionic dyes.

Adsorption of rhodamine B, methylene blue, eosin, and methyl yellow from (semi)aqueous solutions followed pseudo-second-order kinetics, with faster uptake observed for anionic, cationic, and zwitterionic dyes. Weber–Morris analysis indicated that intraparticle diffusion contributes mainly to the initial stage of adsorption, except for eosin, for which it remains the predominant transport mechanism throughout the explored time range. Adsorption isotherms suggested that the process is governed primarily by weak non-covalent interaction, hydrophobic effects, and shape complementarity rather than dye charge, with maximum adsorption capacities of 15, 124, 92, and 167 mg g⁻¹ for methylene blue, rhodamine B, eosin, and methyl yellow, respectively.

Beyond liquid-phase remediation, polymer **7** exhibited a CO₂ uptake of 94.6 mg g⁻¹ at 25 °C and 1 bar, approaching the performance of benchmark porous adsorbents. These findings establish calix[4]tube-based covalent polymers as a versatile new platform for broad-spectrum water purification and gas capture, opening unexplored opportunities for macrocycle-based functional materials.

1. Introduction

The design and synthesis of advanced materials with tailored architectures and distinctive properties represents a rapidly growing research area, fuelled by the demand for novel materials in applications ranging from molecular separations and catalysis to health and energy [1]. Within this context, developing new materials to remove toxic dyes from the environment is globally significant. Sorption has been identified as one of the most effective methods for removing toxic dyes from the environment [2–8]. This approach is particularly relevant given that

approximately 10–15% of the 0.7 million tons of commercially available dyes are discharged annually as aqueous waste from industries such as textiles, cosmetics, and pharmaceuticals [9–11]. Many of these dyes are toxic and environmentally persistent, highlighting the urgent need for effective removal strategies. However, conventional adsorbents often lack the capability to recover dyes upon reuse, leading to additional dye waste [12]. In addition to dye adsorption, gas capture, particularly of CO₂, has emerged as a critical area of focus in the development of multifunctional materials [13,14]. Unlike conventional amine-based sorbents, which are associated with high energy requirements and

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corrosion issues, physisorption presents a more sustainable alternative, enabling low-energy regeneration of the sorbent [15].

Among established classes of macrocyclic molecules, calix[n]arenes stand out because their modular phenolic architecture allows precise control over scaffold size, conformation, and functionality [16,17]. By selectively introducing proper substituents, one can fine-tune their function and modulate their binding affinities for various targets, features that have been exploited for molecular recognition [18–24], drug delivery [25,26], and nanoscale engineering [27–30]. Moreover, computational studies have shown that calixarene-based polymers may be suited to form stacked 2D sheets exhibiting auxetic behaviour [31, 32].

Calixarene-based materials can exhibit binding properties arising from both the intrinsic characteristics of the macrocycle and the architecture of the framework [33,34]. Recently, 2D polymers have been reported for the selective removal of cationic dyes [35,36], oils [37], and organic micropollutants [38] from aqueous media, as well as for iodine capture [39]. In these cases, using alkyne functionalities to connect the macrocyclic building blocks has been linked to enhanced surface area, superhydrophobicity, and adsorption efficiency [36–39]. Additional strategies have included the integration of fluorinated or triazine-based linkers to achieve perfluorooctanoic acid [40] or iodine [41] removal, respectively.

Calixarene-based materials have also been extensively investigated for gas sorption applications. For example, sublimed crystals of *p*-tert-butylcalixar[4]arene have proven effective for the adsorption of greenhouse gases such as CO₂ and methane, accommodating these molecules within the voids of the crystalline lattice [42]. However, soft materials based on non-covalent interactions may suffer from limited structural stability, which has driven the exploration of covalent architectures to harness macrocyclic building blocks for the fabrication of more robust networks [43,44]. In this context, the development of three-dimensional (3D) polymers based on calix[4]arenes remains an underexplored niche due to the synthetic complexity of such systems. One notable example by Pedrini *et al.* employed tetrafunctionalized calix[4]arenes in a Yamamoto coupling strategy to achieve a 3D network, where modulation of the calixarene conformation was crucial to align reactive sites [34]. The resulting material exhibited CO₂ and CH₄ adsorption while selectively excluding nitrogen.

In this study, we aimed to develop an alternative system based on irreversible covalent bonds and dimeric macrocyclic building blocks. Specifically, we utilized the "calix[4]tube" scaffold, composed of two calix[4]arenes bridged at their lower rims by four ethylene linkers [45]. Calix[4]tubes have demonstrated high selectivity for metal ions such as potassium [45–48] and silver [49] within their cryptand-like central cavity, while also binding thallium(I) through their calixarene domains [48]. However, to the best of our knowledge, calix[4]tubes have never been incorporated into polymeric networks, possibly due to their reduced solubility in organic solvents, which complicates further manipulation [49].

Herein, we report the synthesis of polymer 7, fabricated from calix[4]tube building blocks and dialkyne spacers via Sonogashira cross-coupling. The resulting network features a 3D structure with pores in the mesoporous range, which prompted us to investigate its potential as an adsorbent material. This possibility was explored through the removal of toxic dyes from (semi)aqueous media, demonstrating efficient uptake of dyes with different charge states and highlighting the potential of the material for broad-spectrum pollutant sequestration, as supported by kinetic and isotherm analyses. The potential of polymer 7 for CO₂ adsorption was also described, indicating promising prospects for applications in the field of environmental remediation.

2. Material and methods

2.1. General

Commercially available reagents and solvents were bought from Merck, Carlo Erba, TCI Europe, or Fluorochem and used without further purification. Calixarene **1** was synthesized according to literature procedures [50–52]. Tetrahydrofuran, dichloromethane and chloroform were dried over 3 Å molecular sieves, triethylamine was dried over KOH and degassed by bubbling argon. CDCl₃ for NMR was stored over 4 Å molecular sieves. Thin-layer Chromatography (TLC) was run on Merck 5554 silica 60 aluminum sheets. Flash column chromatography was performed on Merck 9385 silica gel 60 (0.040–0.063 mm) for manual purifications, while a CombiFlash NextGen 300 system by TeleDyne ISCO and PUREZZA-Daily Standard Cartridges (silica pore size 60 Å, 50 µm particle size) by Sepachrom were used for automated purifications.

NMR spectra were registered on 400 MHz Bruker Avance 400 or 500 MHz Bruker Avance III HD NMR spectrometers. δ values are expressed in ppm relative to CDCl₃ (7.29 ppm for ¹H and 76.9 ppm for ¹³C) or DMSO-d₆ (2.50 ppm for ¹H and 39.5 ppm for ¹³C). The following abbreviations are used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintuplet, dd = doublet of doublets, td = triplet of doublets m = multiplet, and br s. = broad signal. Solid-state cross-polarization magic angle spinning (CP/MAS) ¹³C NMR spectra of the polymer were recorded on a Bruker Avance NEO 600 (600 MHz) NMR spectrometer equipped with 3.2 mm BBO CP-MAS iProbe at 30 °C with a magic angle spinning rate of 20.0 kHz.

ESI-MS analyses were carried out by using a Waters Acquity Ultra Performance LC instrument equipped with a Waters Acquity SQ Detector and an ESI interface. HR-MS analyses were performed on a Synapt G2-Si HD-DESI, I-Class, M-Class HRMS equipped with an ESI source and a Q-TOF analyzer. Infra-red spectra were measured as KBr discs using a Shimadzu IR-Affinity–1 spectrophotometer. The peak intensities are indicated as strong (s), medium (m), or weak (w). Raman spectra were collected using a Horiba LabRam HR Evolution spectrometer using a 532 nm DPSS Oxxius laser, and 600 (500 nm) grating; calibrated using HORIBA Standard PRO Objective tool with traceable NIST Polystyrene Standard 1921b reference material (SP-RCO); KnowItAll Raman Identification Pro database was used. UV–visible absorption and fluorescence emission spectra were obtained using a Jasco V–650 spectrophotometer and Jasco FP–8300 spectrofluorimeter at room temperature in 10 × 10 × 30 mm Suprasil quartz cuvettes.

Zeta-potential values were measured on a Malvern Zetasizer NanoSeries to estimate the surface charge. SEM measurements were taken using a Carl Zeiss FESEM with a Gemini II Column and the data was analysed using the software SmartSEM®. EDX was carried out using Elect Plus EDS Detector from EDAX Ametek and data was analysed using the software APEX Suite ©. XPS analyses were performed at a photoelectron take-off angle of 45° (relative to the sample surface) with a PHI 5000 Versa Probe Instrument using a monochromatic Al K α X-Ray source excited with a micro-focused electron beam. The binding energy (B.E.) scale was calibrated on the C 1 s peak of adventitious carbon at 285.0 eV. The Brunauer–Emmett–Teller (BET) surface area and the mean pore size (by Barrett–Joyner–Halenda (BJH) model) of the examined samples were determined using a ASAP 2020 instrument. PXRD measurements were carried out using a Stadi MP or Stadi P diffractometer equipped with a curved germanium (111) monochromator and a Mythen 1 K detector, using both Cu-K α 1 radiation (λ = 1.54060 Å) and Mo-K α 1 radiation (λ = 0.70930 Å). Data collection was carried out in Debye–Scherrer geometry and using Hilgenberg capillaries of 0.01 mm wall thickness and 0.50 mm diameter at a temperature of 293 K; calibrated using Si NIST 640d Standard.

Common reagents, solvents, and compounds have been abbreviated as follows: DMF (dimethylformamide); DCM (dichloromethane); THF (tetrahydrofuran); AcOEt (ethyl acetate); NEt₃ (triethylamine); DMAP

(4-dimethylaminopyridine).

2.2. Synthetic procedures

2.2.1. Synthesis of 25, 26, 27, 28 tetraethoxyhydroxyl calix[4]arene (2)

The method was adapted from a literature procedure [53]. Compound **1** (0.59 g, 0.76 mmol) was dissolved in dry diethyl ether (12.5 mL) in a round-bottomed flask, and the mixture was cooled to 0 °C. LiAlH₄ (0.23 g, 6.1 mmol) was added in 3 portions, and the reaction was stirred overnight at room temperature. The reaction was monitored by thin-layer chromatography (ethyl acetate: methanol 9:1; stain: phosphoric acid). The reaction was quenched by the careful addition of 1 N HCl (50 mL) at 0 °C. The white precipitate formed was extracted with diethyl ether (3 × 30 mL). The combined organic layers were washed with 1 N HCl (3 × 25 mL) and dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure, and the crude product was purified by recrystallisation with hexane from dichloromethane/methanol to give **2** as white crystals (0.35 g, 0.58 mmol, 76% yield).

¹H NMR (400 MHz, CDCl₃): δ 6.60–6.70 (m, 12 H, ArH), 4.40 (d, *J* = 13.4 Hz, 4 H, ArCH₂Ar), 4.03 (m, 8 H, OCH₂CH₂), 3.97 (m, 8 H, OCH₂CH₂), 3.27 (d, *J* = 13.5 Hz, 4 H, ArCH₂Ar). Figure S1.

R_f = 0.32 (ethyl acetate: methanol 9:1).

The complete characterization of this compound is reported in literature [53].

2.2.2. Synthesis of 25, 26, 27, 28 tetraethoxytosyl calix[4]arene (3)

The method was adapted from a literature procedure [47]. Compound **2** (0.17 g, 0.28 mmol) and triethylamine (0.14 g, 1.42 mmol) were dissolved in anhydrous dichloromethane (8 mL) in a round-bottomed flask under nitrogen atmosphere. Then, the mixture was cooled to 0 °C for 15 min, *p*-toluene sulfonyl chloride (0.27 g, 1.42 mmol) and a spatula of DMAP (circa 20 mg) were added. The reaction was stirred overnight at room temperature. The reaction was monitored by thin-layer chromatography (hexane: ethyl acetate 6:4) and quenched by pouring the mixture into ice-cold 2 M HCl under vigorous stirring. The organic layer was diluted with dichloromethane (50 mL), washed with 1 M HCl (3 × 25 mL) and brine (2 × 25 mL), dried over anhydrous Na₂SO₄, and the solvent was evaporated under reduced pressure. The pure product was obtained as an off-white solid after recrystallisation from dichloromethane/ethanol (0.28 g, 0.23 mmol, 80% yield).

¹H NMR (400 MHz, CDCl₃): δ 7.79 (d, *J* = 8.0 Hz, 8 H, ArH tosylate), 7.35 (d, *J* = 8.0 Hz, 8 H, ArH tosylate), 6.58 (m, 12 H, ArH), 4.45–4.39 (m, 8 H, OCH₂CH₂), 4.33 (d, *J* = 13.5 Hz, 4 H, ArCH₂Ar), 4.17–4.14 (m, 8 H, OCH₂CH₂), 3.08 (d, *J* = 13.6 Hz, 4 H, ArCH₂Ar), 2.45 (s, 12 H, CH₃ tosylate). Figure S2.

R_f = 0.29 (hexane: ethyl acetate 6:4).

The complete characterization of this compound is reported in literature [47].

2.2.3. Synthesis of calix[4]tube (5)

The method was adapted from a literature procedure [49]. A mixture of calixarenes **3** (0.87 g, 0.71 mmol) and **4** (0.37 g, 0.87 mmol), were dissolved in dry *o*-xylene (300 mL) in a round-bottomed flask. Anhydrous potassium carbonate (1.98 g, 14.3 mmol) was suspended, and the mixture was stirred under nitrogen atmosphere for 5 days. The reaction was monitored by thin-layer chromatography (toluene). The resulting yellow suspension was cooled to room temperature, and the solvent evaporated under reduced pressure. The residue was taken in DCM and the organic layer was washed with brine (3 × 25 mL) and dried over anhydrous Na₂SO₄. After evaporation of the organic solvent, the residue was recrystallised from DCM/ethanol to give calixtube **5** as a yellow to white solid (0.47 g, 0.49 mmol, 69% yield).

¹H NMR (400 MHz, CDCl₃): δ 7.15 (d, *J* = 7.5 Hz, 8 H, ArH meta), 6.91 (t, *J* = 7.5 Hz, 4 H, ArH para), 6.47 (d, *J* = 7.3 Hz, 8 H, ArH meta),

6.40 (t, *J* = 7.5 Hz, 4 H, ArH para), 5.10 (s, 8 H, OCH₂CH₂), 4.61 (d, *J* = 13.0 Hz, 8 H, ArCH₂Ar), 4.47 (s, 8 H, OCH₂CH₂), 3.35 (d, *J* = 13.1 Hz, 8 H, ArCH₂Ar). Figure S3.

R_f = 0.38 (toluene).

The complete characterization of this compound is reported in literature [46,49].

2.2.4. Synthesis of octaiodocalix[4]tube (6)

The method was adapted from a literature procedure [54]. A solution of calixtube **5** (99 mg, 0.10 mmol) in chloroform (15 mL) was added to a refluxing suspension of silver trifluoroacetate (0.55 g, 2.5 mmol) in chloroform (15 mL). The mixture was refluxed for 30 min and then iodine (100 mg, 0.78 mmol) was added in 3 portions until the solution retained a purple colour. The mixture was refluxed overnight and then filtered over Celite. The filtrate was then washed three times with 0.5 M sodium thiosulfate (25 mL × 3), water (25 mL × 3) and brine (25 mL × 1). The solvent was removed in vacuo, and pure **6** was obtained by trituration with acetonitrile. Another aliquot was obtained by washing the Celite with chloroform (100 mL × 3), removing the solvent in vacuo and trituration with acetonitrile. Finally, the yellow solids obtained from the two aliquots were collected (0.092 g, 0.047 mmol, 45% yield).

R_f = 0.95 (toluene: hexane 8:2).

¹H NMR (500 MHz, CDCl₃): δ 7.49 (s, 8 H, ArH), 6.78 (s, 8 H, ArH), 4.95 (s, 8 H, OCH₂CH₂), 4.41 (s, 8 H, OCH₂CH₂), 4.35 (d, *J* = 13.4 Hz, 8 H, ArCH₂Ar), 3.25 (d, *J* = 13.6 Hz, 8 H, ArCH₂Ar). Figure S4.

¹³C NMR (500 MHz, DMSO-*d*₆): δ 31.4, 60.2, 89.6, 125.8, 126.0, 128.5, 128.7, 129.4, 155.2. Figure S5.

IR (KBr disc): cm⁻¹ 3491.16 (br), 3161.33, 2920.23, 2850.79, 1564.27, 1446.61, 1404.18, 1384.89, 1359.82, 1288.45, 1246.02, 1209.37, 1192.01, 1163.08, 1116.78, 1105.06, 1012.63, 921.97, 877.61, 862.18, 844.82, 829.39, 806.25, 615.29. Figure S6.

HR-MS: Calcd. [C₆₄H₄₈I₈K]⁺ 1998.53, found 1998.53.

UV-vis (CH₂Cl₂): λ_{max} 232 nm, 275 nm. Figure S7.

2.2.5. Synthesis of poly[tetraiodo-tetrakis(dialkynyl)calix[4]tube] **7** (polymer **7**)

The method was adapted from a literature procedure [54]. Tris (dibenzylideneacetone)dipalladium(0) (Pd₂(dba)₃) (2.8 mg, 0.0031 mmol, 36 mol% Pd per iodine unit of compound **6**) was weighed in a Schlenk tube, which was previously dried and filled with argon. Dry, degassed triethylamine (4 mL) and P(*t*Bu)₃ (3 μL, 0.012 mmol) were added, followed by calix[4]tube **6** (40 mg, 0.0021 mmol, 0.84 mM) under an atmosphere of argon. Then, a solution of diethynylbenzene (12 mg, 0.095 mmol, 38 mM) in triethylamine (2 mL) were added dropwise under argon to the mixture over 30 min. The Schlenk tube was closed, and the reaction mixture was stirred at 80 °C for 48 h, leading to the formation of a red solid. This was filtered off and washed with methanol, ethanol, dichloromethane, hexane, ethyl acetate, toluene, tetrahydrofuran, chloroform, diethyl ether and dimethylformamide (2 mL each) to give polymer **7** as a dark brown solid.

The polymerisation was also performed at 60 °C, 90 °C, or 120 °C, giving materials with a similar appearance.

Unless otherwise stated, all the characterization reported here and in the main text are referred to polymer aliquots taken from reaction performed at 80 °C.

IR (KBr disc): cm⁻¹ 3055.93, 2967.94, 2930.77, 2201.73, 2179.81, 1597.86, 1398.8, 1369.46, 1185.25, 1104.29, 1008.47, 832.048, 780.429, 736.234, 699.464, 625.57, 529.756, 419.446. Fig. 4a

2.3. N₂-Adsorption/Desorption measurements

The porosity of polymer **7** was determined with adsorption-desorption measurements of N₂ at -196 °C using a Micromeritics ASAP 2020 instrument. The specific surface area values were determined with the Brunauer-Emmett-Teller (BET) methodology [55], whereas the pore size distribution with the Barrett-Joyner-Halenda

(BJH) model [55]. Before the measurements, the samples were degassed at 60 °C overnight.

2.4. CO₂ Adsorption experiments

The CO₂ adsorption tests were carried out in a quartz U-shaped reactor filled with 50 mg of the analyzed material flowing CO₂ (99.999%, 30 mL/min) at atmospheric pressure and room temperature. The CO₂ was monitored with a quadrupole mass spectrometer (Sensorlab VG Quadrupoles) following the $m/z = 44$ signal. The adsorption of CO₂ was evaluated by measuring the ratio between the concentration of CO₂ after the saturation of the material and the initial CO₂ concentration. Before the tests, the materials were pretreated in He flows (50 mL/min) at 150 °C for 1 h. With these experimental conditions, the error was within 3%.

The adsorption capacities were calculated using Eq. 1, where Q is the amount of adsorbed CO₂, w is the weight of the analyzed material (g), q is the CO₂ flow rate (mL/min), t is the saturation time (min), and C_{in} and C_f are the initial and final CO₂ concentrations (mg/mL), respectively [13,56].

$$Q(\text{mg/g}) = [(C_{in} - C_f) \times t \times q] / w \quad (1)$$

The kinetics of CO₂ adsorption were examined using a thermogravimetric analyzer (Linseis STA PT 1600). Prior to analysis, the samples were degassed under a helium flow (50 mL·min⁻¹) at 150 °C for 1 h to remove physisorbed species. Subsequently, carbon dioxide was introduced into the reaction chamber at a flow rate of 30 mL·min⁻¹, and the change in mass of the samples was recorded as a function of time.

The experimental data were fit to both the Linear Driving Force (LDF) and Pseudo-Second Order (PSO) models [57,58].

The linearized form of the LDF model is expressed by Eq. 2, where Q_t and Q_e denote the amount of CO₂ adsorbed per unit mass of the material at time t and at equilibrium, respectively, while the kinetic parameter k_t encompasses all mass transfer resistances to diffusion.

$$\ln(Q_e - Q_t) = \ln Q_e - k_t t \quad (2)$$

The linearized form of the PSO model is described by Eq. 3, where k_s is the rate constant of adsorption, and the other terms are the same as in Eq. 2.

$$t/Q_t = (1/k_s Q_e^2 + t/Q_e) \quad (3)$$

2.5. Surface charge through zeta potential measurement

A 0.03 mg/mL suspension of **7** was prepared in deionised water and sonicated for 15 min. The aqueous suspension was transferred into the cell, and the potential value was measured over 60 cycles at 25 °C.

2.6. Dye adsorption kinetics

In the case of methylene blue, eosin and rhodamine B, a 1 μM x 3 mL dye solution in deionized water was placed in a UV quartz cuvette and its absorbance recorded. A mass of 0.5 mg of **7** was added, and the suspension was stirred at room temperature (25 °C). UV-visible spectra were taken regularly until the absorbance of the solution equilibrated. In the case of methyl yellow, the experiments were performed in the same way but using 5 μM x 3 mL dye solution in 1:1 methanol: deionized water mixtures. A molar extinction coefficient of 67000 M⁻¹ cm⁻¹ ($\lambda = 672$ nm), 106,000 M⁻¹ cm⁻¹ ($\lambda = 554$ nm) and 95,000 M⁻¹ cm⁻¹ ($\lambda = 520$ nm) were used for methylene blue [59], rhodamine B [60], and eosin [61,62] respectively. The molar extinction coefficient of methyl yellow in 1:1 methanol:water mixtures was determined by measuring the absorbance at $\lambda = 409$ nm of dye solutions at variable concentrations (0.005 mM - 0.27 mM range). A molar adsorption coefficient of 23,

695 M⁻¹ cm⁻¹ was calculated from the slope of the linear regression of absorbance versus molar concentration, according to the Lambert–Beer equation (Figure S8). All experiments were carried out in triplicates.

Kinetic data were treated with Eq. 4 to estimate the equilibrium removal efficiency of each dye, where $E\%$ is their percentage removal, C_o is their initial concentration (mg · L⁻¹), and C_e is their equilibrium concentration (mg · L⁻¹).

$$E\% = \frac{(C_o - C_e)}{C_o} \times 100\% \quad (4)$$

The adsorption rate constants were estimated using the linearized pseudo-second order model in Eq. 5, where q_t is the adsorption capacity (mg · g⁻¹) after a denoted time t (minutes), q_e is the adsorption capacity (mg · g⁻¹) at equilibrium, and k_2 is the adsorption rate constant for the pseudo-second-order adsorption (g · mg⁻¹ · min⁻¹).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

The equilibrium dye adsorption capacity (q_e) was in turn calculated using Eq. 6, where C_i and C_f represent the initial and final concentrations of the dye in solution (μM), respectively, V is the volume of the dye solution (L), M_w is the molecular weight of the dye molecule, and m is the mass of the polymer used in the system (g).

$$q_e = \frac{(C_i - C_f) \times V \times M_w}{m} \quad (6)$$

The kinetic data were also analyzed using the Elovich and Weber–Morris models, although both exhibited a lower agreement with the experimental data. (see Section S 4).

2.7. Dye adsorption isotherm

Adsorption isotherms were determined by measuring the equilibrium adsorption capacity (q_e) and equilibrium concentration (C_e) from the absorbance of dye solutions at variable initial concentrations between 0.005 and 1 mM upon incubation with polymer **7**. For each dye, absorbance was measured using the wavelength, extinction coefficients, and solvents indicated in Section 2.6. All experiments were carried out in triplicates.

The experimental data were fit to the Langmuir and Freundlich isotherms.

The Langmuir isotherm is expressed by Eq. 7, where C_e is the equilibrium concentration of the dye (mg L⁻¹), K_L is the Langmuir constant (L mg⁻¹), q_e is the equilibrium adsorption capacity (mg g⁻¹) calculated through Eq. 6 (Section 2.6) and $Q_{\max}$ is the maximum adsorption capacity of polymer **7** in mg g⁻¹.

$$q_e = \frac{Q_{\max} K_L C_e}{1 + K_L C_e} \quad (7)$$

The Freundlich isotherm is instead expressed by Eq. 8, where q_e is the equilibrium adsorption capacity (mg g⁻¹), C_e is the equilibrium concentration in solution (mg L⁻¹), K_F is the Freundlich adsorption constant in (mg/g)(L/mg)^{1/n}, and n is the adsorption intensity.

$$q_e = K_F C_e^{1/n} \quad (8)$$

2.8. Dye recycling

The recycling experiment was investigated using rhodamine B and methylene blue. The UV-vis of a solution of the two dyes was taken. A volume of these solutions (5 mL for rhodamine B and 20 mL for methylene blue) was incubated with 5 mg of polymer **7** for an appropriate time range (20 min for rhodamine B and 3 h for methylene blue). The

polymer was filtered, and the UV-vis of the solution was recorded again to calculate the percentage removal of dye from the solution. The filtered polymer was washed by stirring it in ethanol for 2 h, then filtered off and washed for another 2 h by stirring in acetone. The dye was subsequently dried for a further 2 h at 80 °C and used for another adsorption cycle. This process was repeated to obtain three cycles.

3. Results and discussion

3.1. Polymer synthesis

The synthesis of polymer **7** was achieved as described in Scheme 1. Compound **1** was synthesized as described in documented literature procedures [50–52]. The ester groups at the lower rim were subsequently reduced to alcohols by treatment with lithium aluminium hydride in diethyl ether at room temperature, achieving a yield of 76% (compound **2**) [63]. The resulting hydroxyethyl units were then tosylated by reaction with *p*-toluenesulfonyl chloride in dry dichloromethane to obtain compound **3** in 80% yield [53]. Calix[4]tube **5** was synthesized by the reaction of **3** with precursor **4** via a potassium-templated reaction in xylene [51]. The reaction afforded a yield of 69%, a significant improvement over the reported literature yield of 10% for the same compound [47]. The improved yield may be attributed to the ensured complete dissolution of the reactants in the reaction volume used, as well as an extended reaction time.

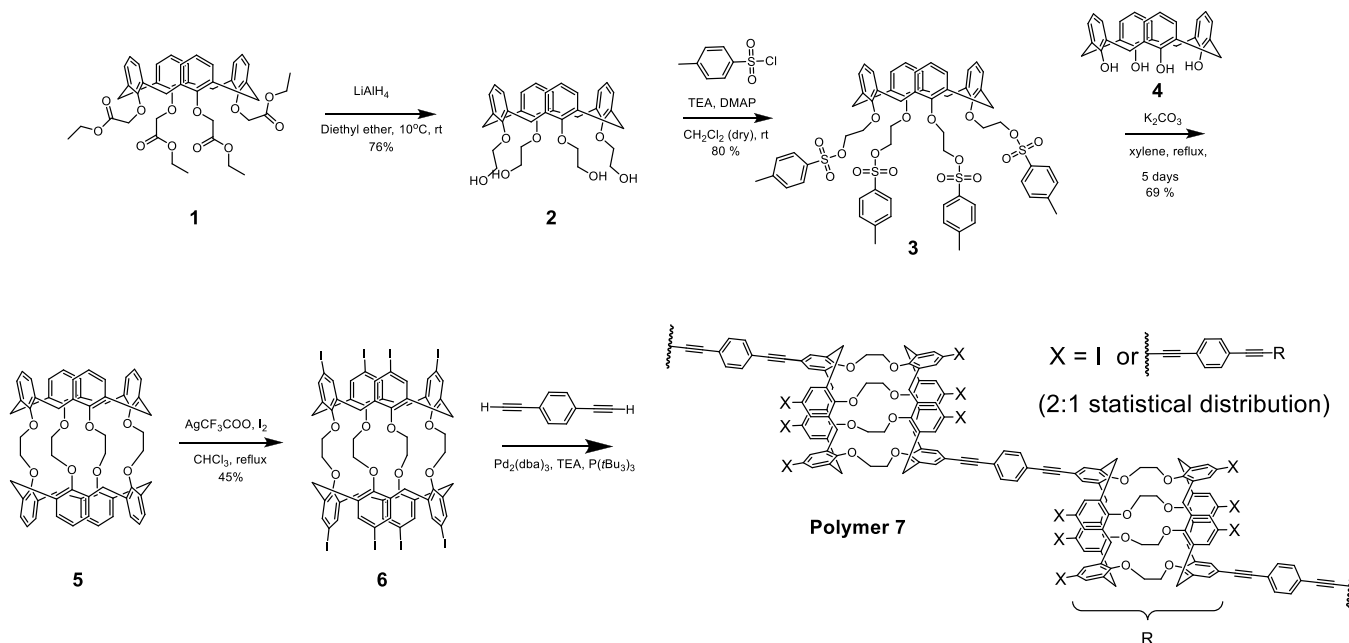
An iodination procedure reported in the literature for monomeric calixarenes [49] was successfully adapted to iodinate all eight positions on the calix[4]tube, affording a yellow solid (compound **6**) in 45% yield after trituration with acetonitrile. The resulting iodinated solid exhibited limited solubility in chloroform, but its solubility was sufficient for characterization and further reactions. The ¹H NMR spectra of compound **6** in CDCl₃ revealed a fully symmetric structure for the complete calix[4]tube and a flattened-cone conformation for its calix[4]arene units, consistent with previous reports in the literature [45–49]. This was evidenced by the observation of singlet pairs corresponding to the ArH and OCH₂ protons and a system of doublets for the ArCH₂Ar bridges of the two macrocyclic units (Figure S4). The compound was further characterised by ¹³C NMR, IR and UV spectroscopy (Figures S5–7).

It was envisaged that if compound **6** was polymerised with a dialkyne

such as 1,4-diethynylbenzene, polymerisation could occur in such a way that each calix[4]tube would be linked to up to eight spacers, which in turn could connect to different calix[4]tubes on the other side. This arrangement would result in a polymeric network with calix[4]tube components separated by rigid linkers that allow for the formation of a three-dimensional structure. The synthesis of the desired network was initially explored using standard Sonogashira conditions [64], which suffered from low conversion due to the difficulties in achieving exhaustive functionalization of compound **6** and the competition with spacer-consuming Glaser side-reactions [65]. These challenges were addressed by adopting harsher conditions and a copper-free Sonogashira protocol [54]. In particular, avoiding the use of copper(I) iodide was deemed useful to prevent Glaser homocoupling of the dialkyne spacer [66]. To balance the reduced reactivity associated with the use of a copper-free reaction, the adapted Sonogashira reaction was performed in neat triethylethylamine [67]. This base was selected over alternatives like morpholine, diisopropylamine, 4-methylmorpholine, and pyridine due to its better ability to dissolve **6**. The poly[tetraiodo-tetrakis(dialkynyl)calix[4]tube] **7**, hereafter indicated as “polymer **7**”, was obtained as a dark brown/black powder (Fig. 1c), which was insoluble in the most common organic solvents. The polymerization reaction was performed at various temperatures (from 60 to 120 °C), using an initial concentration of 5 mM for the starting compound **6**. All reaction temperatures afforded amorphous materials with similar macroscopic appearance. The sample obtained at 80 °C was selected for solid-state characterization, which revealed the formation of a covalent reticular framework with an estimated cross-linking degree of approximately 50% (Section 3.2). Therefore, given the lack of apparent factors leading to selective functionalization of compound **6** during polymerization, polymer **7** is most plausibly described by a statistical distribution of 1, 4-diethynylbenzene linkers, corresponding on average to two linker units and two unreacted iodine substituents per face of each calix[4]tube building block. These substituents may adopt either a vicinal arrangement on adjacent aromatic rings or a distal arrangement on opposite rings, as depicted in Scheme 1 and Fig. 1.

3.2. Polymer characterisation

The structure of the product polymer was investigated through a



Scheme 1. Synthesis scheme for compound **6** and polymer **7**, where R represents calix[4]tube repeating units with an estimated cross-linking degree of approximately 50% and a statistical distribution of dialkynyl bridges and unreacted iodine substituents.

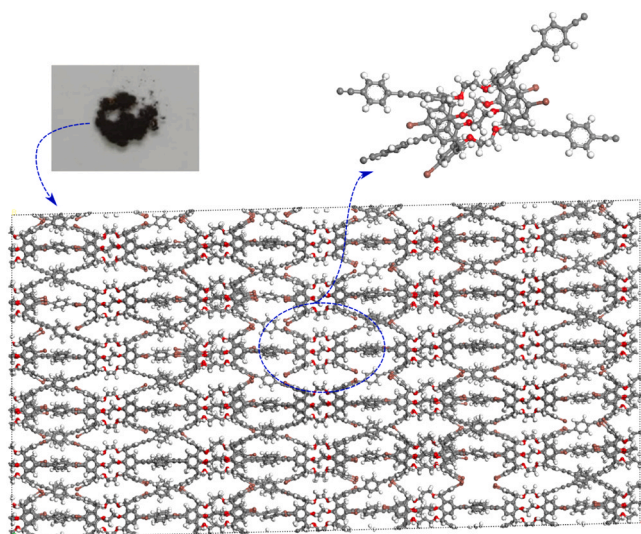


Fig. 1. Proposed structural model of the calix[4]tube-based polymer **7**. Theoretical packing model showing the statistical incorporation of 1,4-diethynylbenzene linkers between calix[4]tube units, with an average of two linkers and two unreacted iodine substituents per calix[4]tube face. The enlarged structure illustrates a representative unit with possible vicinal or distal iodine substitution patterns. Inset: photograph of the obtained polymer.

series of techniques in the solid-state, as its pronounced insolubility prevented any characterization in solution. The PXRD analyses of **7** suggested that the bulk product was predominantly amorphous, as indicated by the characteristic broad peak at low 2θ values as well as the high background in the baseline (Fig. 2a). This feature was consistent across reactions conducted at moderate to high temperatures (60 °C, 80 °C, 90 °C, and 120 °C under solvothermal conditions, Figure S9). These findings are in agreement with previous reports on the synthesis of calix[4]arene-based polymers in the literature [36,37]. The amorphous nature of the synthesized product might be due to the inherent challenges of achieving multiple C-C couplings at eight distinct sites of **6**, as well as to the possibility that two or more alkyne spacers reacted with the same calix[4]tube rather than with separated ones, leading to disordered bulk morphologies. In addition, the residual mobility of the calix[4]tube units, deriving from the oscillation of their aryl ring around the Ar-CH₂-Ar bridges, might further hinder the formation of a crystalline system. Nevertheless, peaks belonging to the calix[4]tube **6** and of 1,4-diethynylbenzene were not observed in the diffraction pattern of the polymer, excluding contamination from unreacted starting materials (Figure S10). Thermogravimetric analysis (TGA) revealed that **7** exhibits increased thermal stability compared to **6**, with the polymeric product remaining stable up to 350 °C, whereas the starting calix[4]tube **6**

decomposes at circa 300 °C (Figure S11).

The bulk morphology of polymer **7** was also analyzed via scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX). SEM images showed that **7** consisted of clumps fused together (Fig. 2b and Figure S12a). EDX spectra confirmed that the networks predominantly comprised carbon and oxygen, with residual iodine suggesting unreacted sites on some calix[4]tube (Figure S12b). X-ray photoelectron (XPS) spectroscopy was carried out to verify the nature of the chemical bonding (Fig. 3 and Table S1). The XPS survey of the calix[4]tube **6** exhibited signals corresponding to C, O, and I (Fig. 3a i). The C 1s region (Fig. 3a ii) consists of two main components: the first one centred at 284.6 eV associated with carbon atoms of the hydrocarbon skeletal backbone C=C/C-C of the calix[4]tube. The second component at 286.3 eV can be associated with the C-O groups of these units. I 3d region clearly shows the I 3d_{5/2} and 3d_{3/2} doublet at 620.1 eV and 631.6 eV, respectively (Fig. 3a iii). These values are higher than those typical of metal iodide and are consistent with the presence of iodine bonded to carbon atoms.

The XPS spectra of polymer **7** revealed signals due to C, O and I, mirroring those of its calix[4]tube component **6**. However, the I 3d_{5/2-3/2} intensities of **7** at 620.1 eV and 631.6 eV are lower than for **6** (Table S1), indicating polymerization (Fig. 3b). Analysis of the XPS data allowed to estimate the extent of cross-linking yielded by the Sonogashira reaction, by comparing the I/C and I/O atomic ratios of polymer **7** with those of its calix[4]tube precursor **6**. Taking into account the additional carbon atoms introduced by the bridging units during polymerization, analysis of the I/C ratio indicated a conversion of approximately 48% (Table S1, Equations S1–S4), while the I/O ratio, for which the linker does not contribute additional oxygens, yielded a conversion of approximately 54% (Table S1, Equations S5). Overall, these results support an average degree of conversion of about 50%. This value is consistent with the formation of a three-dimensional hyper-cross-linked structure. Pd(II) peaks observed in the spectra of **7**, are instead ascribable to catalyst-derived palladium species embedded in the material, accounting for circa 4.5% of surface element abundance (Table 1, Figure S13). When compared to **6**, the C 1s region of **7** showed a negligible contribution of the C-O groups due to the high amount of aliphatic and aromatic carbon atoms in its structure, providing additional evidence of polymerization (Fig. 3b ii).

Fourier transform infrared (FTIR) spectroscopy was employed to characterize the molecular structure of the polymer (Fig. 4a). Notably, the characteristic sharp band near 3300 cm⁻¹, corresponding to the terminal alkyne -C-H stretch of 1,4-diethynylbenzene (Figure S14), was absent in the spectrum of the polymer. Furthermore, a new band emerged at approximately 2158 cm⁻¹, which is attributed to the asymmetric -C≡C- stretch, confirming the formation of the desired di-alkyne bridges within the polymer. Raman spectra (Fig. 4b) showed a G-band at approximately 1585 cm⁻¹, attributed to the vibrations of sp²-hybridized carbon atoms. A band at around 1350 cm⁻¹ corresponds to

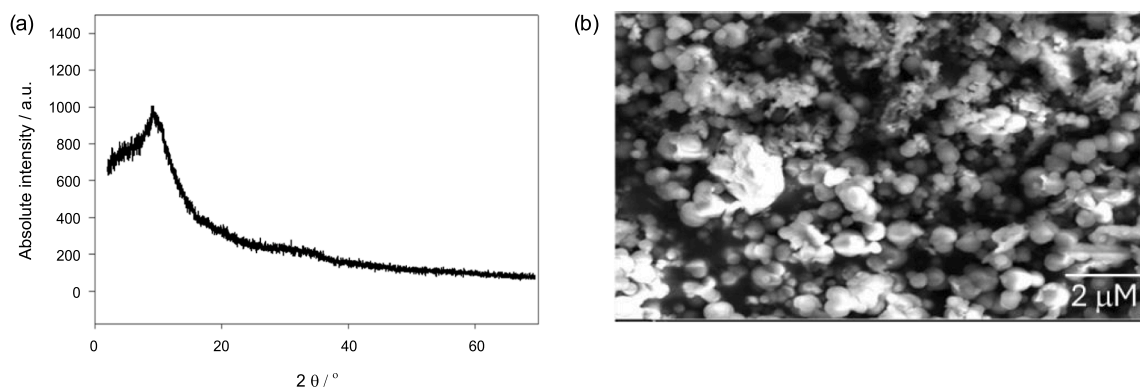


Fig. 2. (a) PXRD pattern collected using Cu-K α 1 radiation and (b) SEM analyses of polymer **7**.

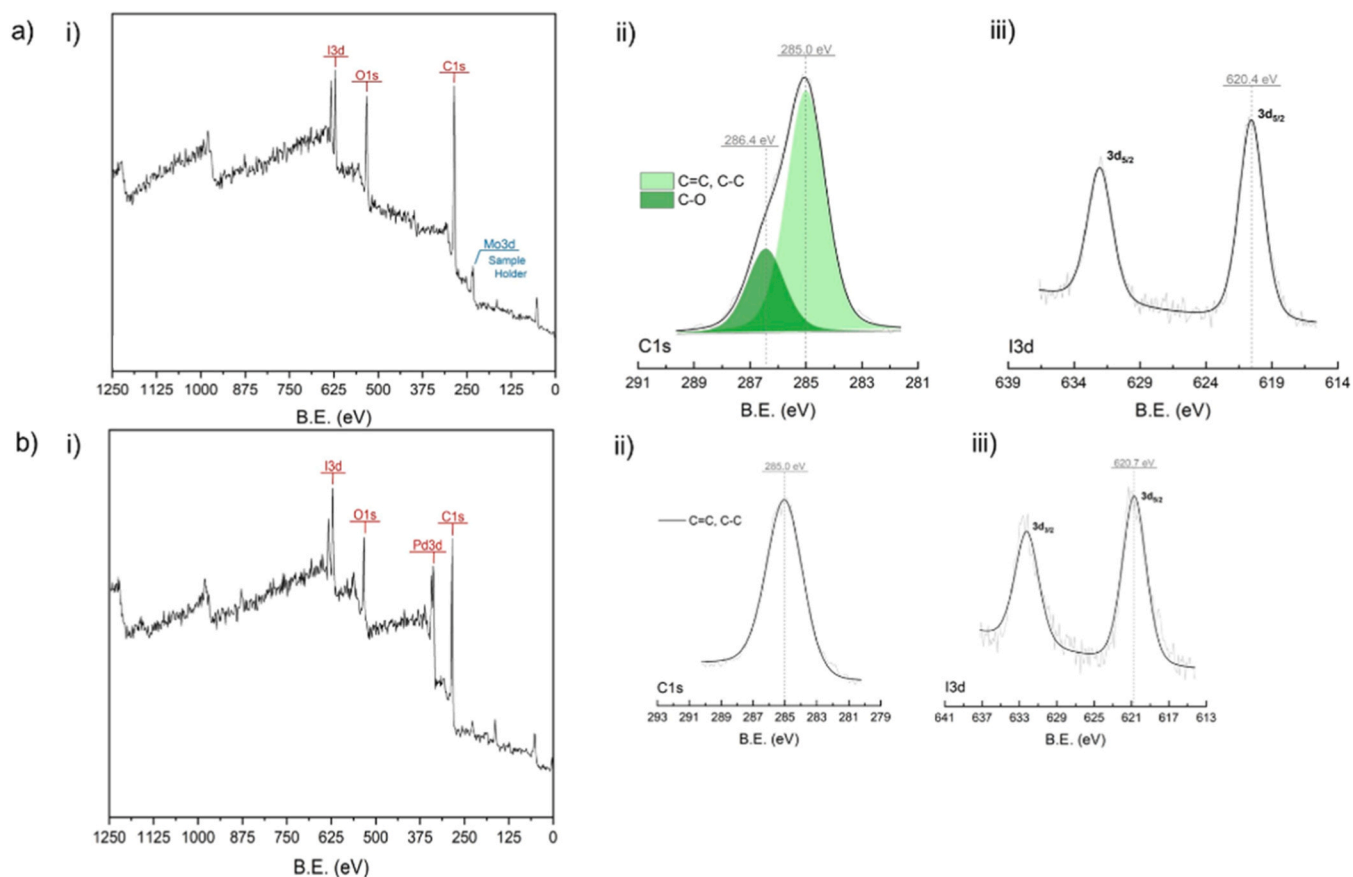


Fig. 3. XPS analyses of (a) calix[4]tube 6 and (b) polymer 7. Panels (i) report full-range spectra, while panels (ii) and (iii) show high-resolution scan spectra for C 1 s and I 3d, respectively.

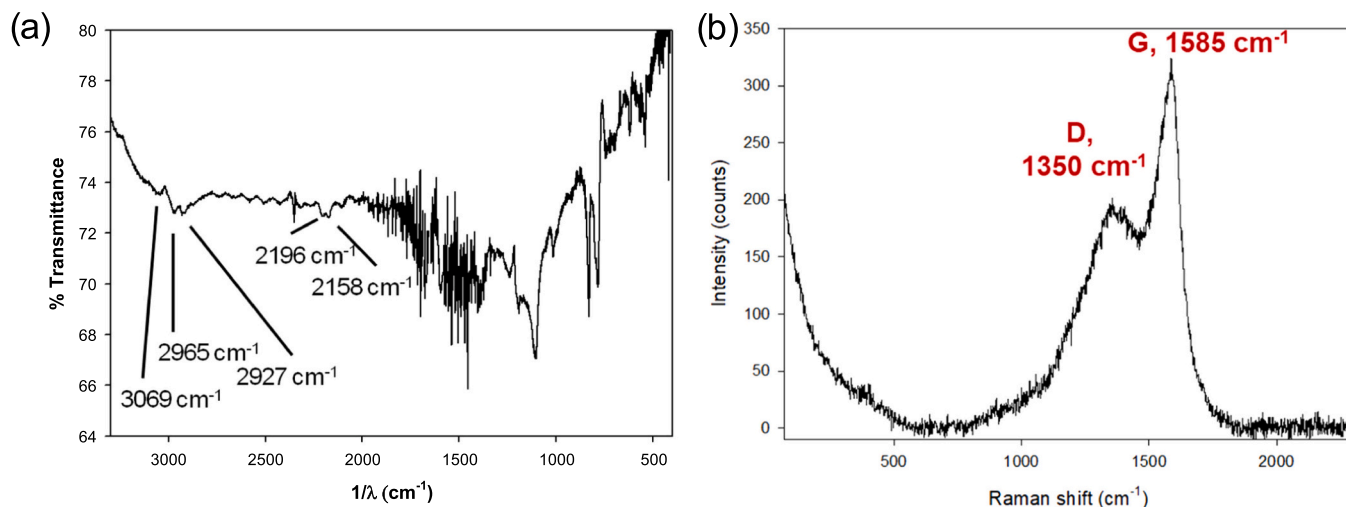


Fig. 4. (a) IR spectrum and (b) Raman spectrum of polymer 7 (baseline corrected).

structural defects within the polymers. The Raman spectra are consistent with those reported for other calixarene-based polymers in the literature [35–37].

Further characterisation of the molecular structure of the polymer was obtained using solid-state cross-polarization magic angle spinning (CP/MAS) ^{13}C NMR spectroscopy (Fig. 5). The chemical shift values observed at approximately 155 ppm are attributed to phenolic quaternary aromatic carbons located at the lower rim of the calix[4]arene macrocycles. Signals in the 120–140 ppm region correspond to aromatic

carbons within the polymeric framework, including those from both the calix[4]tube and 1,4-diethynylbenzene building blocks. In this range, the lower field signal was assigned to quaternary aromatic carbons (labelled b* in Fig. 5), whereas the other was assigned to carbons in *meta* to the phenolic positions or belonging to the spacer units (labelled b in Fig. 5). Spectral broadening suggests the presence of multiple aromatic signals due to slight variations in local environments, potentially arising from packing and conformational differences, or minor disorder in the solid state. The peak observed around 30 ppm is associated with the

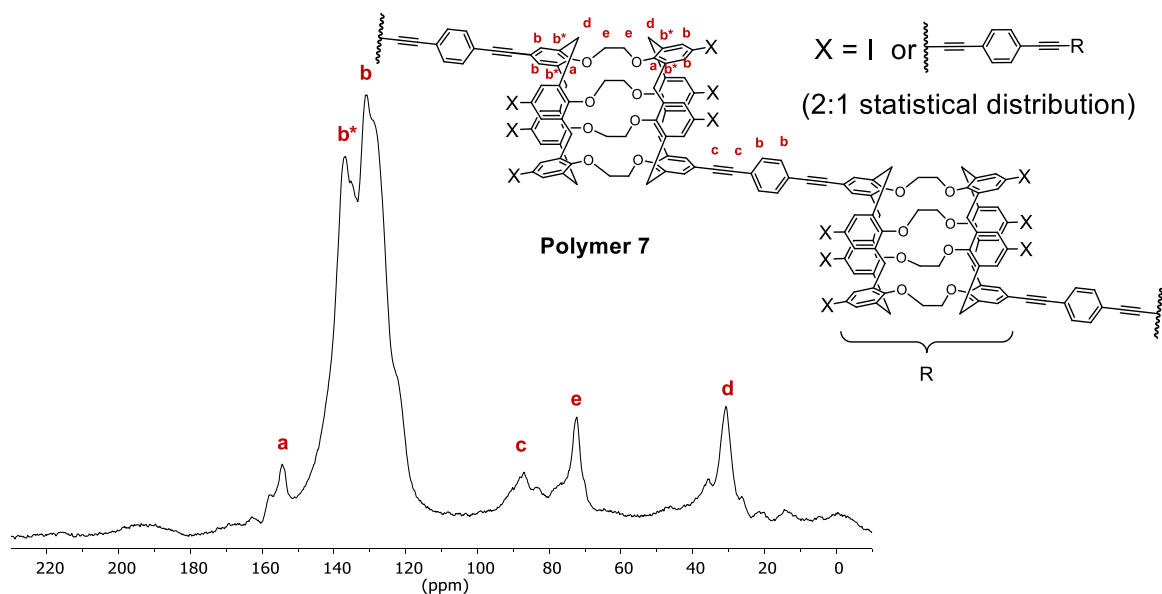


Fig. 5. ^{13}C CP/MAS NMR spectrum of polymer 7 and corresponding peak assignments.

aliphatic methylene (Ar-CH₂-Ar) moieties connecting the phenolic rings of each calix[4]arene macrocycle, while the resonances corresponding to the ethylene (O-CH₂CH₂-O) and alkyne (-C≡C-) carbons appear at circa 70 and 90 ppm, respectively. The signal at circa 90 ppm could also include contributions of aromatic carbon bound to unreacted iodine units. Similar results were obtained via direct polarisation magic angle spinning (DP-MAS) ^{13}C NMR spectroscopy (Figure S15).

3.3. Evaluation of gas adsorption potential

The porosity of polymer 7 was evaluated through N₂ adsorption/desorption measurements. The resulting N₂ sorption isotherm was classified as Type IV with an H3-type hysteresis loop (Fig. 6a), consistent with desorption behaviors described by the IUPAC classification system [72]. Furthermore, the average pore diameter of approximately 6 nm (Fig. 6b) falls within the 2–50 nm range that defines mesopores according to IUPAC nomenclature [73], confirming the mesoporous nature of the material. Specific surface area calculations using the Brunauer–Emmett–Teller (BET) model yielded a value of 35.1 m²/g. These results suggest a low-to-moderate porosity polymeric network composed

of aggregates of plate-like particles, probably featuring slit-shaped pores and large interparticle voids. The relatively modest BET surface area may result from partial framework densification and/or limited microporosity development during polymer formation. Mesoporous materials have been widely explored for the capture of environmental pollutants and greenhouse gases, [8,37] suggesting that polymer 7 could be suited for this application despite its relatively modest BET surface area. In fact, the combination of available mesopore/interparticle voids and favourable adsorbate–framework interactions may compensate for the lower surface area, contributing to the efficient adsorption of both gases (see below) and dyes (see Section 3.4).

Gas adsorption was explored using CO₂ as a model adsorbate, owing to the significant attention this gas has received in the field of environmental remediation. The adsorption performance was evaluated by flowing CO₂ through a reactor containing compound 7 at atmospheric pressure and room temperature, measuring the ratio between the initial CO₂ concentration and that after saturation of the material (Eq. 1, Section 2.4). The performance of polymer 7 was first compared with that of standard BEA zeolite (Fig. 7a), which is widely employed in industrial applications for the adsorption of VOCs (volatile organic compounds),

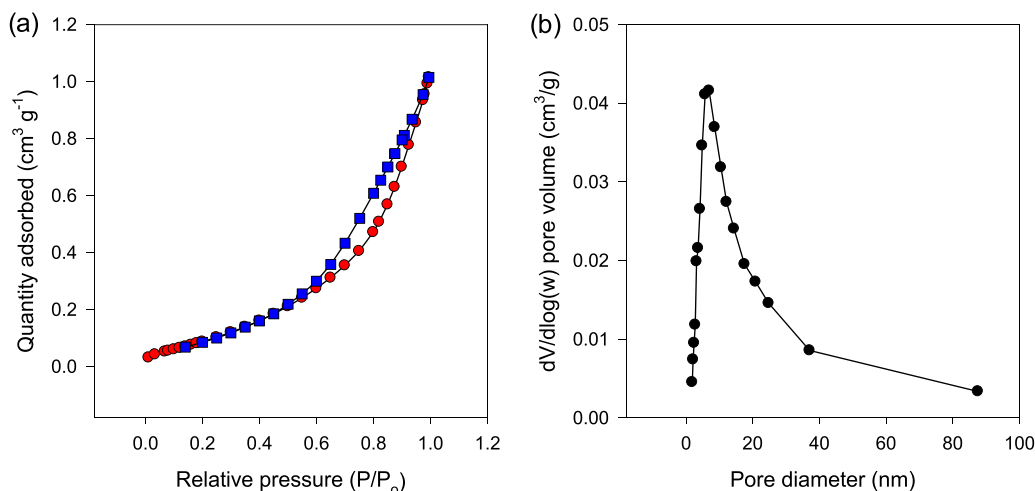


Fig. 6. (a) N₂ uptake isotherm at 77 K (red circles represent adsorption while blue squares represent desorption). (b) The pore size distribution plot for 7 as determined from the N₂ adsorption/desorption isotherm.

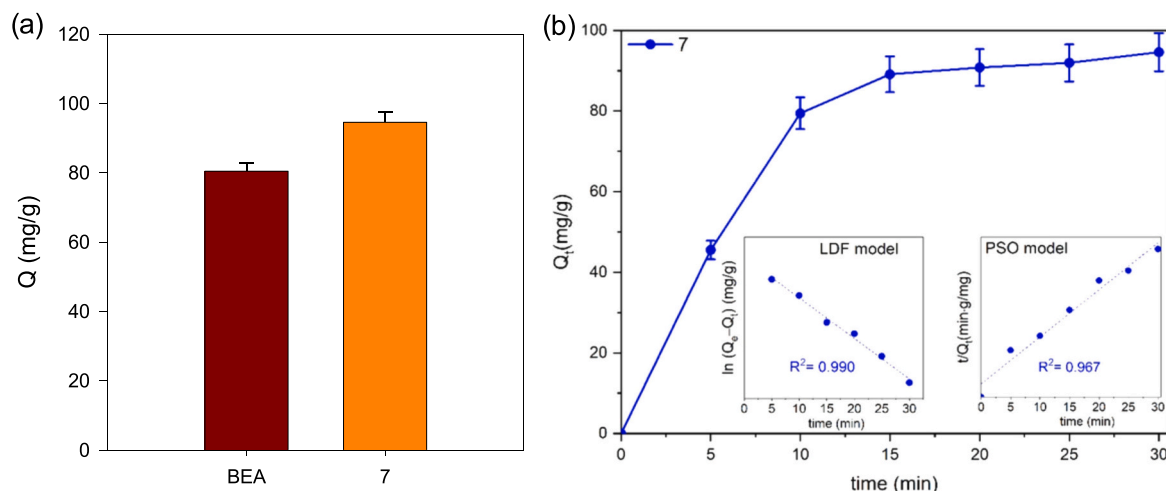


Fig. 7. (a) The CO₂ adsorption capacity of **7** in comparison with standard zeolite BEA. (b) CO₂ adsorption kinetics on polymer **7**. The experimental data (points) and the fit (dashed lines) were represented in the insets with the LDF and the PSO models.

nitrogen oxides, and CO₂ capture [39,50,63,64,74,75]. Interestingly, polymer **7** exhibited a CO₂ uptake capacity ($Q = 94.6 \text{ mg g}^{-1}$) approximately 14% higher than that of BEA zeolite ($Q = 80.5 \text{ mg g}^{-1}$) under the investigated conditions. Furthermore, although direct comparison with literature data must be treated cautiously since adsorption conditions, activation procedures, pressure, temperature, and pretreatments vary considerably among different studies, the performance of polymer **7** remains comparable or even superior to several recently reported MOFs and porous organic polymers listed in Table 1. Importantly, the results highlight that CO₂ capture performance is not exclusively determined by the specific surface area of the material. Indeed, pore accessibility, material morphology, and the presence of functional groups capable of interacting with CO₂ can play a more decisive role in the adsorption process. This aspect is evident, for example, in the case of

Table 1

Comparison of the CO₂ adsorption performance of Polymer **7** and other representative materials.

Sample	BET surface area (m ² /g)	CO ₂ adsorption conditions	Activation steps	Q CO ₂ (mg/g)	ref.
polymer 7	35.1	CO ₂ (99.999%, 30 mL/min) atmospheric P, room T	He flows (50 mL/min) at 150 °C for 1 h	94.6	this work
MOF 1	198	clean air as a diluting gas mixed with pure CO ₂ (99.9%), atmospheric P, 25 °C	Drying in a furnace at 110 °C for 2 h by N ₂ gas	44.0	[44]
MOF 2	1139	dry ambient temperature (25 °C), atmospheric P, CO ₂ (90 mL/min)	pre-treating under N ₂ at 150 °C for 16 h	45.0	[68]
MOF 3	343.96	CO ₂ flow (>99.995%), 1 bar, 298 K	Heating at 110 °C under vacuum for 12 h	109.1	[69]
MOF 4	965	CO ₂ flow, 1 bar, 298 K	Degassing at 523 K at a pressure of 10 ⁻⁵ torr for 12 h	330	[70]
CB[6]-Funct	277	CO ₂ (99.999%, 30 mL/min) atmospheric P, room T	He flows (50 mL/min) at 150 °C for 2 h	88.4	[71]

Mg-MOF-74 film (MOF 4), which exhibits the best adsorption performance among the compared materials (Table 1) despite not possessing the highest BET surface area. On the contrary, the Zirconium-Based Nanoporous UiO-66 MOF (MOF 2) exhibited a considerable surface area (1139 m² g⁻¹) but one of the lowest CO₂ capture capacities among the compared materials (45.0 mg g⁻¹, Table 1). Therefore, despite its relatively low surface area, the high CO₂ adsorption activity of polymer **7** may arise from a combination of its mesoporosity, which could facilitate the diffusion and accessibility of CO₂ molecules, and the functional units constituting its framework, which may promote interactions with the gas.

For polymer **7**, the adsorption kinetics were investigated by fitting the experimental data to both the Linear Driving Force (LDF) model and the Pseudo-Second Order (PSO) model [57,58], as illustrated in Fig. 7b. The LDF model describes the adsorption rate as being proportional to the number of available surface sites suitable for adsorption (Eq. 2, Section 2.4), primarily governed by physisorption, while the PSO model assumes that adsorption occurs predominantly through chemisorption (Eq. 3, Section 2.4). As shown in Fig. 7b, the LDF model exhibits a superior fit to the experimental data ($R^2=0.99$) for the sample under investigation, indicating that the interaction between polymer **7** and CO₂ should be primarily governed by reversible physisorption rather than chemisorption.

3.4. Adsorption of dyes

Prior to evaluating compound **7** for the adsorption of water-soluble dyes, the surface charge potential of the polymer was assessed to identify suitable candidates. The polymer surface was determined to be nearly neutral (average value of $-0.179 \pm 3.52 \text{ mV}$, Figure S16), contrasting with the strongly negative values obtained for materials based on calix[4]arenes featuring free phenolic units on their scaffold [35]. However, in our case, these positions were masked with ethylene linkers during the synthesis of calix[4]tube **6**, and polymer formation did not involve the incorporation of charged units, thereby explaining the formation of a neutral framework. Therefore, polymer **7** was investigated in water solutions containing dyes with a variety of charges, using methylene blue, eosin, rhodamine B, and methyl yellow as typical cationic, anionic, zwitterionic, and neutral dyes, respectively.

The potential of polymer **7** was initially evaluated in terms of adsorption kinetics, which, unless otherwise stated, were investigated through UV-Vis analysis of 1 μM x 3 mL aqueous dye solutions where 0.5 mg of polymer **7** was suspended for appropriate time intervals. Kinetic data were then treated with Eq. 4 (Section 2.6) to estimate the

equilibrium removal efficiency of each dye (E%), while the adsorption rate constants (k_2) were estimated using a linearized pseudo-second order model (Eq. 5, Section 2.6). In all cases, the kinetic data were well described by the selected kinetic model, as evidenced by the high correlation coefficient observed for each dye (Fig. 8, panels a-d iii, Table S2).

In the case of methylene blue, featuring a positively charged structure (Fig. 8a) [76], the dye absorbance in the tested spectral range decreased rapidly over time (Fig. 8a i), suggesting polymer-mediated adsorption from the aqueous solution. The plot of normalized dye concentration as a function of time showed that the polymer was saturated within 100 min (Fig. 8a ii), as indicated by the absence of further absorbance variations beyond this time. Comparison between the final and initial absorbance values at the same wavelength revealed an equilibrium dye removal efficiency of 89% at room temperature. The fitting of the experimental data to Eq. 5 yielded a k_2 of 0.418 g mg⁻¹ min⁻¹, confirming the tendency of polymer 7 for rapid dye adsorption (Fig. 8a iii).

High adsorption efficiency was also observed for rhodamine B, a toxic dye frequently used in the textile industry, which predominantly exists in zwitterionic form (Fig. 8b) [77]. UV-vis spectra taken over time revealed a progressive reduction of rhodamine B absorbance in the investigated spectral range, indicating effective removal of the dye by polymer 7 (Fig. 8b i). The time-course concentration decrease revealed that polymer saturation occurred after approximately 50 min (Fig. 8b ii), corresponding to a dye removal efficiency of 93% at room temperature and an adsorption rate constant of 0.321 g mg min⁻¹ (Fig. 8b iii).

Conversely, a fast but less efficient adsorption was observed when polymer 7 was challenged with eosin, a negatively charged water contaminant (Fig. 8c) [78]. In fact, despite the rapid decrease in eosin absorbance upon exposure to polymer 7 (Fig. 8c i), with adsorption equilibrium being reached within approximately 100 min and a pseudo-second-order rate constant of 2.20185 g mg⁻¹ min⁻¹ (Fig. 8c iii), the removal efficiency reached only 37% (Fig. 8c ii). This result indicates that, although eosin adsorption proceeds rapidly, the overall adsorption capacity of polymer 7 toward this dye is lower than that observed for methylene blue and rhodamine B.

To broaden the scope of its adsorption profile, polymer 7 was further evaluated with methyl yellow, which was used as an example of neutral carcinogenic dye [79]. Due to its low water solubility and extinction coefficient relative to the other dyes, the experiments were conducted at higher initial concentration and using a partly organic medium. Precisely, a 5 µM solution of methyl yellow in a 1:1 methanol/water mixture was treated with 0.5 mg of polymer 7, resulting in a gradual decrease in concentration over 50 min (Fig. 8d i, corresponding to an E% of 86% (Fig. 8d ii) and a k_2 of 0.0951 g mg⁻¹ min⁻¹ (Fig. 8d iii). Although the combination of high adsorption efficiency and a relatively low kinetic constant appear to deviate from the trend observed for the other dyes, comparisons should consider the different experimental conditions employed (*vide infra*).

Methylene blue was selected as a model dye to investigate adsorption at higher concentrations and to preliminarily assess the practical applicability of the tested material for water remediation. Adsorption kinetics were therefore repeated using a 50 µM dye solution, resulting in the removal of approximately half of the dye at equilibrium (E% = 50%). The process exhibited a k_2 of 0.029 g mg⁻¹ min⁻¹, as determined by linear regression of the experimental data using the linearized pseudo-second-order kinetic model (Fig. S17, Table S2). Considering that dye concentrations in industrial wastewater typically range from 10 to 200 mg/L, [80] corresponding to approximately 30–600 µM for methylene blue, this additional experiment demonstrates that polymer 7 remains effective at concentrations being commonly encountered in real wastewater streams.

Alternative data treatment was performed using the Elovich (Equation S6) and Weber–Morris (Equation S7) kinetic models for all dyes, generally showing lower agreement with the experimental data. In

particular, application of the linearized Elovich equation yielded poorer correlation coefficients for all dyes, indicating that this model was less suited to describe the adsorption kinetics (Figure S18, Table S3). Rhodamine B, methylene blue, and methyl yellow deviated from the canonical Weber–Morris behaviour, displaying multiple profiles with two or more distinct slopes (Figure S18 ii, Table S4). Nevertheless, the initial part of their plots exhibited good linearity, suggesting that this model adequately describes the early stage of adsorption, with diffusion rate constants (k_{id}) of 0.0203, 0.203 and 0.245 mg g⁻¹ min^{-1/2} for methylene blue, rhodamine B and methyl yellow, respectively. In contrast, eosin showed a linear correlation over the entire experimental time range, from which an intraparticle diffusion constant of 0.001 mg g⁻¹ min^{-1/2}.

Subsequently, the behaviour of polymer 7 in dye removal was investigated through adsorption isotherms studies. This was achieved by determining the equilibrium adsorption capacity (Q_e) and equilibrium concentration (C_e) from the absorbance of dye solutions after incubation with polymer 7 across suitable ranges of initial dye concentrations (0.005 – 1.0 mM). Once again, experiments involving methyl yellow required the use of 1:1 water/methanol mixtures as a solvent, while the other dyes were investigated in a fully aqueous medium. The experimental data were then fit to the Langmuir isotherm (Eq. 7, Section 2.7), with plots of Q_e against C_e showing a hyperbolic trend for all dyes (Fig. 9) and the maximum adsorption capacities (Q_{max}) being determined by nonlinear regression analysis as the asymptotic values of the fitted curves. In the case of methylene blue and rhodamine B, the fitting yielded Q_{max} values of 15 and 124 mg g⁻¹ for polymer 7 (Fig. 9a, b), respectively, which approach or even surpass those reported for commercially available activated carbon (Q_{max} = 21.5–91 mg g⁻¹ for methylene blue [81] and 58–87 mg g⁻¹ rhodamine B [82]). Q_{max} values of 92 mg g⁻¹ and 167 mg g⁻¹ were instead obtained for eosin (Fig. 9c) and methyl yellow (Fig. 9d) based on the corresponding adsorption isotherms. The Freundlich isotherm (Eq. 8, Section 2.7) was also considered as an alternative model, but it showed a poorer fit to the experimental data (lower r^2 and higher χ^2) and was therefore less suitable for describing the behaviour of polymer 7 (Figure S19, Table S5).

Although direct elucidation of the adsorption mechanism would require dedicated spectroscopic characterization and/or molecular modelling studies, the adsorption kinetics and equilibrium data provide useful insights into the adsorption process.

The Weber–Morris model adequately described only the initial adsorption stage for most dyes, indicating that intraparticle diffusion contributes to the early uptake but is not the only rate-limiting step throughout the process. The subsequent deviations from linearity suggest that additional transport and/or adsorption processes become increasingly important as equilibrium is approached [83]. Eosin represented the only exception, for which the Weber–Morris model satisfactorily described the experimental data over the investigated time range. At equilibrium, the better agreement with the Langmuir model than with the Freundlich model supports adsorption occurring predominantly through monolayer coverage of relatively homogeneous adsorption sites rather than multilayer adsorption with non-uniform affinity for the adsorbent surfaces.

Overall, the experimental data do not indicate an obvious correlation between dye charge and adsorption by polymer 7. Among the fully water-soluble dyes, methylene blue and rhodamine B exhibited comparable adsorption kinetics despite their different ionic character, whereas eosin was adsorbed more rapidly but reached a lower removal efficiency. Likewise, the equilibrium capacities did not parallel the kinetic behaviour, with the highest Q_{max} values obtained for eosin and rhodamine B and substantially lower values for methylene blue.

Therefore, the results are more consistent with adsorption arising from the combined action of several weak non-covalent interactions that do not strictly depend on dye charge. Considering the aromatic near-neutral framework of polymer 7, hydrophobic interactions, π - π stacking, CH- π interactions and, where applicable (e. g. rhodamine or

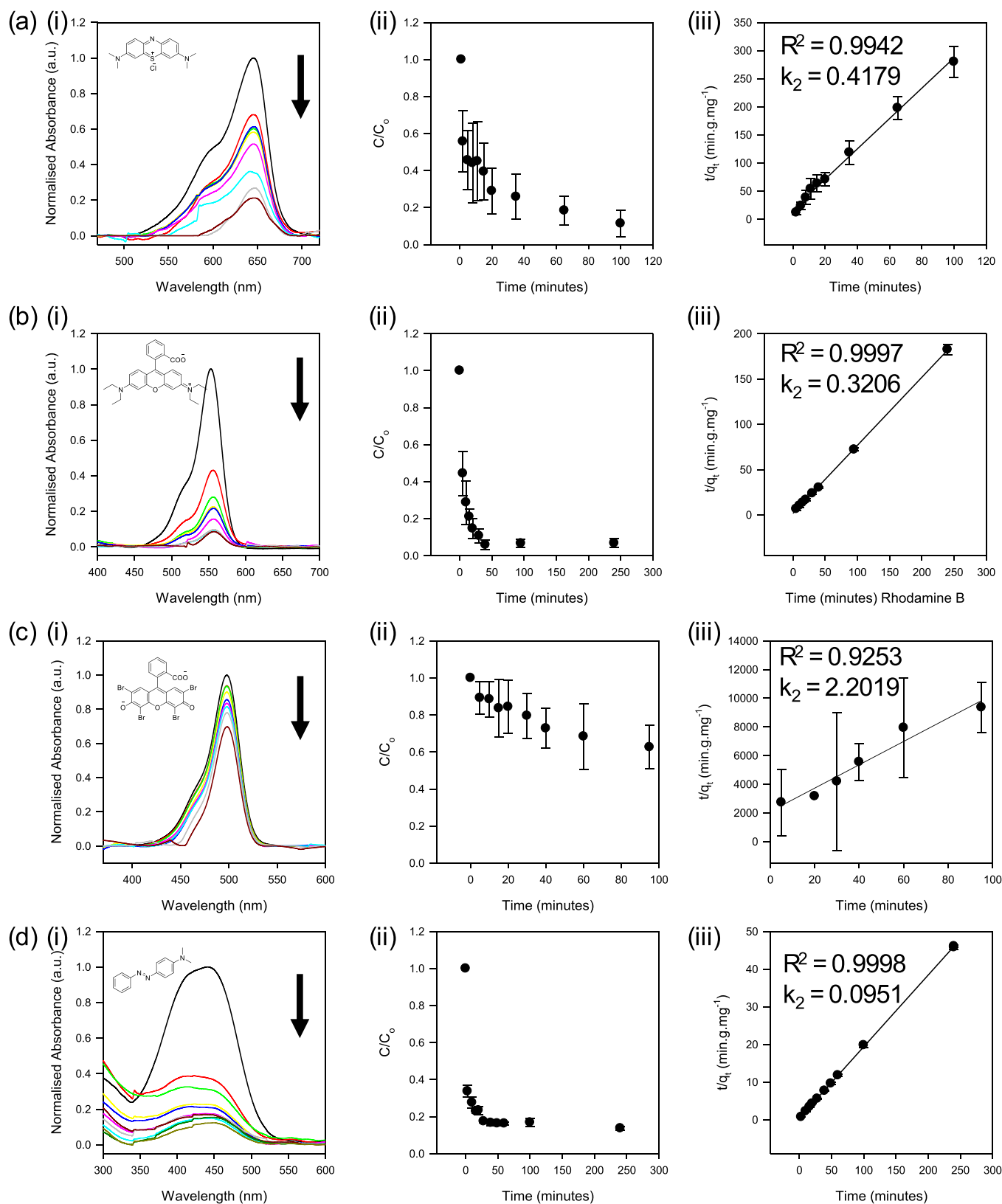


Fig. 8. (i) Normalised UV-vis spectra (baseline corrected) of (a) methylene blue, (b) rhodamine B, (c) eosin, (d) methyl yellow solutions in the absence (black lines) and in the presence of polymer 7 over time. (ii) The change in the concentration of each dye over time. (iii) Linear plots to pseudo-second-order kinetics.

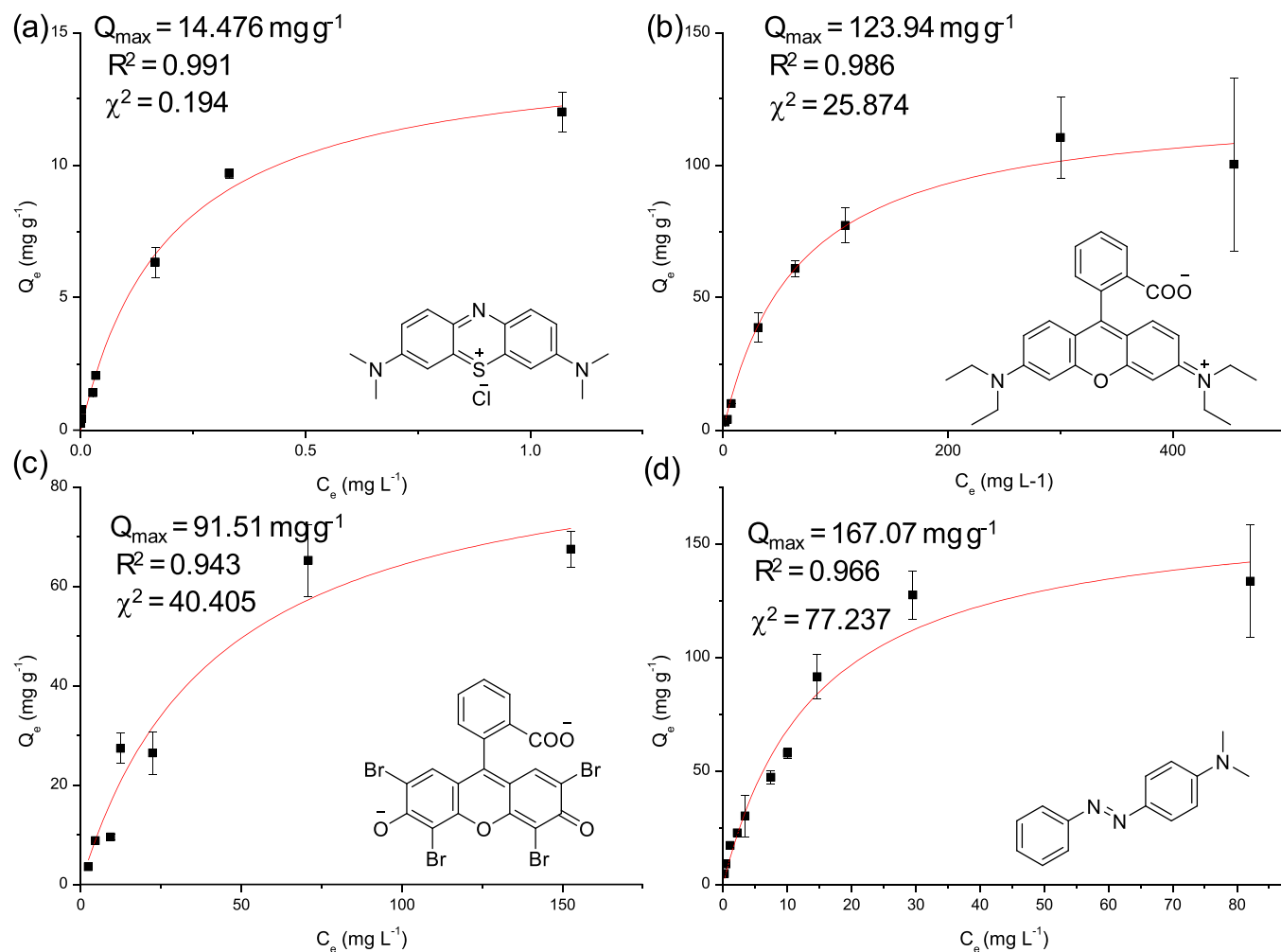


Fig. 9. Langmuir adsorption isotherm of polymer 7 for (a) methylene blue, (b) rhodamine B, (c) eosin, (d) methyl yellow. Q_e (mg g^{-1}) is the amount of dye adsorbed at equilibrium and C_e (mg L^{-1}) is the equilibrium dye concentration.

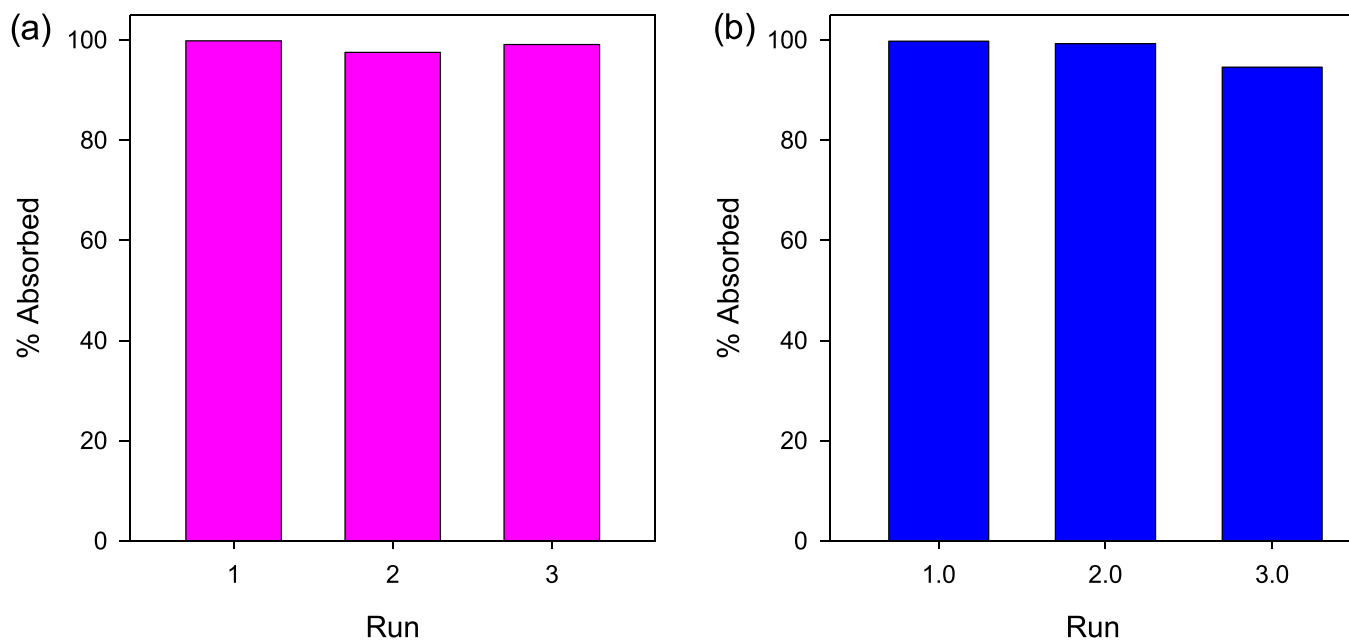


Fig. 10. Recycling of 7 for (a) rhodamine B and (b) methylene blue at a concentration of $1 \mu\text{M}$ in water. The dye-adsorption procedure was carried out over three consecutive cycles with no measurable loss in adsorption capacity.

methylene blue), cation- π interactions may be plausible contributors, potentially complemented by hydrogen bonding involving the phenolic oxygens of the calix[4]tube units. The porous architecture of polymer **7**, comprising intrinsic calix[4]tube cavities together with permanent pores and interparticle voids, may further contribute through size and shape complementarity between the dyes and the adsorption sites. Although these hypotheses are compatible with the experimental observations, confirmation will require dedicated structural investigations.

Although methyl yellow was investigated in a 1:1 water/methanol mixture, its high adsorption capacity further supports a significant contribution of hydrophobic interactions. Despite being less competitive than pure water, this solvent mixture remains highly polar and protic, making it reasonable that these interactions are important to promote the adsorption of this neutral dye.

Finally, the recyclability of polymer **7** was investigated using rhodamine B and methylene blue. Under the conditions described in Section 2.8, 99% of both rhodamine B and methylene blue was removed from the solution in the first cycle of adsorption. Given the suggested relevance of hydrophobic interactions in driving the adsorption process, polymer regeneration was performed using organic solvents able to disrupt these non-covalent interactions. Accordingly, the material was sequentially washed with ethanol and acetone (i.e. solvents of progressively lower polarity) until the supernatant became colourless, indicating complete dye desorption. After washing and drying, the polymer was re-used without significant loss of adsorption efficiency (Fig. 10), as evidenced by the removal of 98% and 99% of rhodamine B and 99% and 95% of the methylene blue during two additional adsorption cycles. The recyclability of the polymer likely arises from the reversible character of the non-covalent interactions established between the dye and the adsorption sites, further supporting the idea that hydrophobic effects make a significant contribution to dye adsorption. Moreover, the straightforward regeneration of the material highlights the practical advantages of integrating calix[4]tubes into a multifunctional polymer matrix for water purification and separation.

4. Conclusions

To the best of our knowledge, this work delivers the first three-dimensional covalent network built from calix[4]tube macrocycles. By employing a copper-free Sonogashira coupling between an octaiodinated calix[4]tube and 1,4-diethynylbenzene spacers, we have fabricated an amorphous yet thermally robust polymer featuring mesopores ($\phi \approx 6$ nm) and a specific surface area of $35.1 \text{ m}^2 \text{ g}^{-1}$. The resulting material combines near-neutral surface charge ($\zeta \approx -0.18 \pm 3.52 \text{ mV}$) with a semi-rigid, hydrophobic architecture, imparting broad-spectrum adsorption performance which finds applications in the removal of various dyes from (semi)aqueous solutions and in room-temperature CO_2 uptake, rivalling standard BEA zeolite and metal-organic frameworks for these two applications, respectively. These synergistic features, i.e. mesoporosity, binding sites integrating pores, macrocyclic units and interstitial spaces, structural stability, and near-neutral surface charge, determine the versatility of polymer **7** as a multifunctional adsorbent for both aqueous pollutants and greenhouse gases. The high CO_2 uptake efficiency of polymer **7**, comparable or superior to that of commercially available adsorbents, highlights the potential of calix[4]tube-based materials in decarbonisation technologies. Moreover, the polymer exhibits versatile adsorption toward dyes with different charge states, thus representing a promising alternative to charge-selective adsorbents. These results not only affirm the potential of polymer **7** in dye removal but also suggest wider applicability in the remediation of other organic pollutants, such as pharmaceuticals and oils, from aqueous environments. More broadly, this study highlights the promise of calix[4]tube-based porous frameworks as versatile functional materials for both water purification and gas adsorption. Future studies on CO_2 capture will focus on adsorption/desorption stability, CO_2 selectivity over competing gases, and temperature-dependent adsorption isotherms to

further elucidate the gas adsorption mechanism and assess the practical potential of polymer **7** for carbon capture applications. For dye adsorption, dedicated experimental investigations combined with computational modelling will be undertaken to elucidate the molecular factors governing uptake.

CRediT authorship contribution statement

Cardona M.A.: Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization; **Abdilla R.:** Investigation; **Pulviranti L.:** Investigation; **Scicluna M.C.:** Investigation; **Fiorenza R.:** Investigation, Data curation; **Makuc D.:** Investigation; **Grima J.N.:** Resources; **Baisch U.:** Methodology; **Condorelli G.G.:** Methodology, Investigation, Data curation; **Casnati A.:** Funding acquisition; **Volpi S.:** Writing – review & editing, Supervision, Data curation; **Gatt R.:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mtcomm.2026.115720.

Data Availability

Data will be made available on request.

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