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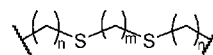
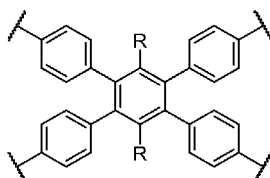
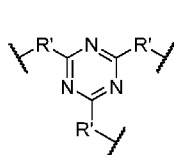
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(54) Title: POROUS ORGANIC MATERIALS FOR IODINE REMEDIATION IN WATER



(57) **Abstract:** An ionic porous organic framework (H_COF-7) is provided to remove iodine residues (I₂ and I⁻), demonstrating high breakthrough volumes and wide working temperatures. The organic frameworks may be made from various components/monomers having the structures: "A groups," and "B groups." The A groups can be linked to B groups, and the A groups can be linked to other A groups via a counterion (e.g., NO₃⁻) or crosslinking groups having the structure:.

POROUS ORGANIC MATERIALS FOR IODINE REMEDIATION IN WATER

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Application No. 63/353,413, filed June 17, 2022, the disclosure of which is incorporated herein by reference.

5 STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[0002] This invention was made with government support under grant 1844920 awarded by the National Science Foundation. The government has certain rights in the invention.

BACKGROUND OF THE DISCLOSURE

10 **[0003]** Access to clean water has been a continuous demand for public health for thousands of years in human society, and civil engineered water treatment plants have been constructed worldwide for water purification. However, the need for disinfected water is still critical in areas such as remote places, extreme environments, locations with severe poverty, and outer space stations. In these places, iodine (I₂) is an effective broad-spectrum
15 antimicrobial reagent used for water disinfection. For example, the United States Environmental Protection Agency recommends iodine as the emergency biocide for drinking water. The International Space Station employs iodine (in the form of I₂/KI) in the portable water dispenser (PWD) system for disinfection. The residual iodine in water (5-16 mg/L or ppm) after the treatment needs to be removed due to its negative metabolic effects and its
20 astringent taste. These iodine residues are currently removed by a composite column packed with active charcoal/ion-exchange resin. However, the narrow working temperature of these columns (e.g., below 50 °C for the resin used for I⁻ exchange) and the limited iodine/iodide breakthrough capacity stipulates the development of porous materials with wide working temperature (up to 90 °C), good iodine removal efficiency at low concentrations (~5 ppm),
25 and high breakthrough capacities.

[0004] Iodine is widely used as an antimicrobial reagent for water disinfection in the wilderness and outer space, but residual iodine and iodide need to be removed for health reasons. Currently, it is challenging to remove low concentrations of iodine and iodide in water (~5 ppm). Furthermore, the remediation of iodine and iodide across a broad
30 temperature range (up to 90 °C) has not previously been investigated.

[0005] Recently, a series of porous materials such as metal-organic frameworks (MOFs), covalent organic frameworks (COFs), and porous organic polymers (POPs) have

been developed for iodine removal. In most cases, these porous materials demonstrated high capacitive iodine adsorptions at high iodine concentrations in the vapor phase, and limited progress had been achieved for low iodine residues. High capacitive iodine removal in the aqueous environment using hydrogen-bonded crosslinked organic frameworks, COFs, and POPs at ambient conditions has been previously shown. In these investigations, I^- is introduced to stabilize I_2 in water via the $I_2 + I^- \rightleftharpoons I_3^-$ equilibrium, but porous organic materials remove iodine (I_2) only at high concentrations ($\gg 100$ ppm) from water. These concentrations are much higher than the iodine residual levels (5-16 ppm) in treated drinking water.

10 SUMMARY OF THE DISCLOSURE

[0006] The present disclosure provides a nitrate dimer-directed synthesis of a single-crystalline ionic hydrogen-bonded crosslinked organic framework (HcOF-7). HcOF-7 removes iodine and iodide species in water efficiently through halogen bonding and anion exchange, reducing the total iodine concentration to 0.22 ppm at room temperature. Packed HcOF-7 columns were employed for iodine/iodide breakthrough experiments between 23 and 90 °C, and large breakthrough volumes were recorded (≥ 18.3 L/g). The high iodine/iodide removal benchmarks recorded under practical conditions make HcOF-7 a promising adsorbent for water treatment.

[0007] The present disclosure also uses melaminium moieties to construct an ionic HcOF-7 for simultaneous iodine and iodide removal. HcOF-7 adsorbs iodine through halogen bonding interactions and iodide via anion exchange. First, molecular precursor **1** possessing four allyl-melamine arms was synthesized and co-crystallized with nitric acid to form $1 \cdot 4H^+ \cdot 4NO_3^-$. Then, these melaminium-based single crystals were converted to single-crystalline ionic HcOF-7 (Figure 1) through a photo-irradiated thiol-ene single-crystal to single-crystal (SCSC) transformation. The porous architecture was stabilized after thiol-ene crosslinking. The crystal structure of HcOF-7 revealed that it is the first porous organic network connected through nitrate dimers. These nitrate dimers are hydrogen-bonded with melaminium moieties in HcOF-7. HcOF-7 removes I_2 and/or I^- species in aqueous solutions, and the NO_3^-/I^- anion exchange is more effective when $I_2 \cdot HcOF-7$ is used. At a 5 ppm dosing concentration of I_2/I^- , HcOF-7 reduced the residual I_2/I^- concentrations to 0.22 ppm at 23 °C and 0.45 ppm at 90 °C, demonstrating excellent iodine/iodide removal efficiencies at a wide range of temperatures. HcOF-7 columns showed high breakthrough volumes when iodinated water (5ppm of I_2/I^-) was passed through, recorded as 20.0 L/g at 23 °C and 18.3 L/g at

90 °C. These benchmarks are significantly higher than any reported porous framework materials or porous polymers, demonstrating HcOF-7's promising potential for practical considerations.

[0008] Also provided is an ionic hydrogen-bonded crosslinked organic framework HcOF-7 through anion dimer-directed assembly followed by thiol-ene single-crystal to single-crystal transformation. HcOF-7 shows significantly enhanced chemical stability compared to its molecular precursor crystal, which is attributed to the added ethanedithioether crosslinks. This ionic HcOF-7 possesses 1D porous channels, strong iodine-binding melaminium moieties, and nitrate dimers for anion exchange. As a result, HcOF-7 uptakes iodine and iodide collectively in the aqueous environment under a wide range of working temperatures (23–90 °C). HcOF-7 demonstrates excellent total iodine residue removal capability at low concentrations of iodine and iodide—the total residual iodine concentration was measured as low as 0.22 ppm from an intake of 5 ppm iodine/iodide solution. Packed HcOF-7 columns showed large breakthrough volumes (18.3 to 20.3 L/g) in the dynamic adsorption experiments at different temperatures. The benchmarks for iodine and iodide removal were set using porous organic framework materials at different temperatures. This feature is particularly important for potential uses in extreme environments like the wild field or space stations.

BRIEF DESCRIPTION OF THE FIGURES

[0009] For a fuller understanding of the nature and objects of the disclosure, reference should be made to the following detailed description taken in conjunction with the accompanying figures.

[0010] **Figure 1.** Schematic representation of a synergistic I₂/I⁻ removal in water using an ionic HcOF-7.

[0011] **Figure 2.** (a) The chemical structure of **1**, (b) its solid-state structure, and (c) super-structure. (d) The chemical structure of **1**•4H⁺•4NO₃⁻, (e) its solid-state structure, and (f) super-structure. (g) The nitrate dimer-directed hydrogen-bonding joint formed between two repulsive nitrate anions and four melaminium arms. (h) The *flu* topology of **1**•4H⁺•4NO₃⁻ crystal. (i) Highlighted void space of **1**•4H⁺•4NO₃⁻ crystal.

[0012] **Figure 3.** (a) Synthesis of HcOF-7 via an SCSC thiol-ene crosslinking. (b) Stacked FT-IR spectra of **1**, **1**•4H⁺•4NO₃⁻ crystal, and HcOF-7. (c) Stacked Raman spectra of **1**•4H⁺•4NO₃⁻ crystal and HcOF-7. (d) Stacked ¹³C solution NMR spectrum of **1**•4H⁺•4NO₃⁻ in DMSO-*d*₆ (bottom, 150 MHz, 298 K) and solid-state ¹³C cross-polarization magic angle

spinning NMR spectrum of HcOF-7 (100 MHz, 298 K). (e) Simulated and experimental PXRD profiles of $1 \cdot 4\text{H}^+ \cdot 4\text{NO}_3^-$ crystal and HcOF-7, respectively.

[0013] **Figure 4.** (a) Crystal structure of HcOF-7 with dithioether crosslinkages and nitrate dimer highlighted in ball-stick model. (b) Overlaid structures of $1 \cdot 4\text{H}^+ \cdot 4\text{NO}_3^-$ crystal and HcOF-7. Hydrogen atoms are omitted for clarity. (c) Covalent connections in HcOF-7. Nitrate anions and hydrogens are omitted for clarity. (d) Highlighted void spaces of HcOF-7.

[0014] **Figure 5.** (a) Time-dependent iodine/triiodide adsorption of HcOF-7 measured at different temperatures (23, 40, 50, 90 °C) using UV-Vis spectroscopy by monitoring the absorption band at 292 nm. Inset: fitted reaction rate versus the inverse temperature. (b) The weight-increased amounts of HcOF-7, CHOP-7, and activated carbon after total uptake measured at different temperatures. (c) The I^- exchange efficiency measured using HcOF-7 and $\text{I}_2 \cdot \text{HcOF-7}$ samples (0.1–0.3 g/g of I_2 per HcOF-7). The confidence coefficient p was obtained using Tukey's honest significance test. (d) Measured concentrations of total residual iodine (input: $\text{I}_2 + \text{KI}$, 3.5 + 1.5 ppm) before and after adsorption using HcOF-7 (6 mg) in deionized (DI) water in the presence of NO_3^- (5 ppm), H_2PO_4^- (5 ppm), SO_4^{2-} (20 ppm), Cl^- (80 ppm), HCO_3^- (60 ppm), and their mixture. (e) Experimental setup of the temperature-controlled iodine/iodide breakthrough analysis. Iodinated DI or tap water ($\text{I}_2 + \text{KI}$, 3.5 + 1.5 ppm) was pumped into a customized steel pre-column (d: 50 × 1: 220 mm) and heated to the desired temperatures under continuous flow (5 mL/min). After passing through the HcOF-7 column (d: 4.5 × 1: 27 mm), the deiodinated water was collected by a fraction collector. (f) The total residual iodine ($\text{I}_2 + \text{I}^-$) concentrations measured in the breakthrough experiments. Each column was packed with 240 mg of HcOF-7, activated carbon, or mixed-bed activated carbon/anion exchange resin.

[0015] **Figure 6.** (a-c) The *pcu* topology of 1_{crystal} crystal along the *a*-, *b*-, and *c*- axis, respectively. Monomer 1 monomer is defined as a six-connected node for constructing the hydrogen-bonded network.

[0016] **Figure 7.** (a) Molecular structure of 1_{crystal} (b) The head-to-head and side-to-side hydrogen-bonding interactions of DAT functional groups with chemical formula diagram. (c) The hydrogen-bonding connection between 1 (d) The 2×2×2 packing of 1_{crystal} viewed along the *a*-axis (void space: 10.8 %).

[0017] **Figure 8.** ^1H NMR spectra (500 MHz, DMSO-*d*₆, 298 K) of 1 and $1 \cdot 4\text{H}^+ \cdot 4\text{NO}_3^-$ crystal.

[0018] **Figure 9.** TGA profiles of 1, $1 \cdot 4\text{H}^+ \cdot 4\text{NO}_3^-$ crystal, and HcOF-7 (heating rate: 10 °C /min) under an N₂ atmosphere.

[0019] Figure 10. PXRD profiles of the simulated $1 \cdot 4H^+ \cdot 4NO_3^-$ crystal and the experimental data of $1 \cdot 4H^+ \cdot 4NO_3^-$ crystal after being immersed in different solvents for 24 h and dried in the open air for 12 h.

[0020] Figure 11. (a) Overlaid molecular structures and (b) the $1 \times 1 \times 1$ packing of 1 crystal and $1 \cdot 4H^+ \cdot 4NO_3^-$ crystal.

[0021] Figure 12. (a) Asymmetric unit and (b) the molecular structure of $1 \cdot 4H^+ \cdot 4NO_3^-$ crystal (c-f) The allyl groups with the distance between 4 to 10 Å in $1 \cdot 4H^+ \cdot 4NO_3^-$ crystal, which could possibly be crosslinked by EDT.

[0022] Figure 13. (a) Molecular structure of $1 \cdot 4H^+ \cdot 4NO_3^-$ crystal (b) The $2 \times 2 \times 2$ packing of $1 \cdot 4H^+ \cdot 4NO_3^-$ crystal viewed along the a -axis with crosslinking active sites highlighted as red balls. (Void space: 35.6%) (c) The nitrate dimer connecting four $1 \cdot 4H^+$ monomers with nitrate dimer highlighted. (d) The mode of interactions between nitrate dimer with melaminium functional groups. (e) The nitrate dimer connecting a 2D chain in $1 \cdot 4H^+ \cdot 4NO_3^-$ crystal.

[0023] Figure 14. (a-c) The *flu* topology of $1 \cdot 4H^+ \cdot 4NO_3^-$ crystal along the a -, b -, and c -axis, respectively. The nitrate dimer is defined as a four-connected linker and $1 \cdot 4H^+$ as a six-connected node for constructing the hydrogen-bonded network.

[0024] Figure 15. ^1H NMR spectra (500 MHz, DMSO- d_6 , 298 K) of $1 \cdot 4H^+ \cdot 4NO_3^-$ crystal after solvent exchange by THF and cyclohexane.

[0025] Figure 16. ^1H NMR spectra (500 MHz, DMSO- d_6 , 298 K) of $1 \cdot 4H^+ \cdot 4NO_3^-$ crystal after EDT diffusion. The ratio of $[1 \cdot 4H^+]:[EDT]:[consumed\ allyl]:[unreacted\ allyl]$ is measured as 1:2.2:3:5.

[0026] Figure 17. ^1H NMR spectrum of HcOF-7 soluble residue after crosslinking. Single crystals of HcOF-7 (~5 mg) were added to 0.5 mL boiling DMSO- d_6 to extract any unreacted species. Only trace organic residues were noticed in the ^1H NMR spectrum.

[0027] Figure 18. PXRD profiles of HcOF-7 after being immersed in various solvents for 24 h, followed by vacuuming (8.0 Pa) for 24 h.

[0028] Figure 19. (a) The asymmetric unit of HcOF-7 containing half of the **1**-like moiety, two nitrate anions, one and half of cyclohexane, and dithioether linkages. Three of the four alkylthioether chains are disordered over two positions, and the disordered components are labelled. (b) Distances of a partially assigned thioether linkage (one S and one C atoms) to the nearby alkyl carbon atoms in the HcOF-7 crystal structure. The C-C distance between the C34A-C19 is 6.65 Å. Since these carbon atoms are located on the pore surface, they are disordered over several positions. Although there was no discovery of

discrete electron densities to bridge the partially assigned thioether linkage, the short distance between C34A and C49 (3.75 Å) suggests a disordered linkage connecting C19 and C34A.

[0029] **Figure 20.** Different crosslinking connections in HcOF-7. (a) A fraction of the EDT is intramolecularly connected. (b) Intermolecular connections in HcOF-7, where one arm extends the network along the 100 axis (blue colored) and another extends along the 001 axis (cyan colored). (c) The packing structure of HcOF-7 viewed along the 100 axis. EDT is shown in the ball-and-stick model, and other atoms are shown in capped stick model. Hydrogen atoms, solvent molecules, and anions are omitted for clarity.

[0030] **Figure 21.** (a-c) The $(4^4.8^{16}.12^8)(4)_4$ topology of HcOF-7 along the *a*-, *b*-, and *c*- axis, respectively. The protonated pentaphenyl core and the dithioether moieties are defined as an eight-connected node and two-connected linkers, respectively.

[0031] **Figure 22.** FT-IR spectra of compound **1**, **1**-EDT polymer, CHOP-7, and HcOF-7.

[0032] **Figure 23.** (a) TGA profiles of **1** and **1**-EDT polymer (heating rate: 10 °C /min) under an N₂ atmosphere. (b) TGA profiles of CHOP-7 and HcOF-7 (heating rate: 10 °C /min) under an N₂ atmosphere.

[0033] **Figure 24.** CO₂ sorption isotherm of HcOF-7 recorded at 298 K.

[0034] **Figure 25.** MeOH sorption isotherm of HcOF-7 recorded at 298 K.

[0035] **Figure 26.** (a) UV/Vis spectra of the standard iodide solution after 10 min reaction time with Leuco-crystal violet and N-chlorosuccinimide. (b) The linear fit of absorbance at 592 nm of standard iodide solution after 10 min of reaction time with Leuco-crystal violet and N-Chlorosuccinimide.

[0036] **Figure 27.** UV/Vis spectra of the 0.07 mM KI solution, 0.07 mM KNO₃ solution, and the mixture of (0.07 mM KI + 0.07 mM KNO₃).

[0037] **Figure 28.** The UV/Vis spectra of an I₂ solution (0.59 mM, H₂O/MeOH = 99:1) in the presence of 0-12 equivalents of KI.

[0038] **Figure 29.** The UV/Vis absorbances of I₂ (0.59 mM) with 0-12 equivalent of KI measured at 292 nm and 354 nm. The equilibrium constant calculated as 816 M⁻¹ and 782 M⁻¹ at 292 nm and 354 nm, respectively. The averaged equilibrium constant is 792 ± 20 M⁻¹.

[0039] **Figure 30.** The time-dependent UV/Vis absorbance at 292 nm of I₂/I⁻ aqueous solution (0.12 mM I₂, 0.5 mM KI, 292 nm) in the presence of 10 mg HcOF-7 under different temperatures.

[0040] **Figure 31.** (a) Time-dependent UV/Vis spectra of I₂/KI solution (I₂: 0.12 mM, KI: 0.50 mM, 15 mL) in presence of HcOF-7 (10 mg) under 23 °C. (b) Pseudo-first-order

fitting of total iodine adsorption at 23 °C by monitoring the absorption band at 292 nm, $k = (2.59 \pm 0.01) \times 10^{-4} \text{ s}^{-1}$.

[0041] Figure 32. (a) Time-dependent UV/Vis spectra of I₂/KI solution (I₂: 0.12 mM, KI: 0.50 mM, 15 mL) in presence of HcOF-7 (10 mg) under 40 °C. (b) Pseudo-first-order fitting of total iodine adsorption at 40 °C by monitoring the absorption band at 292 nm, $k = (9.06 \pm 0.14) \times 10^{-4} \text{ s}^{-1}$.

[0042] Figure 33. (a) Time-dependent UV/Vis spectra of I₂/KI solution (I₂: 0.12 mM, KI: 0.50 mM, 15 mL) in presence of HcOF-7 (10 mg) under 50 °C. (b) Pseudo-first-order fitting of total iodine adsorption at 50 °C by monitoring the absorption band at 292 nm, $k = (1.34 \pm 0.03) \times 10^{-3} \text{ s}^{-1}$.

[0043] Figure 34. (a) Time-dependent UV/Vis spectra of I₂/KI solution (I₂: 0.12 mM, KI: 0.50 mM, 15 mL) in presence of HcOF-7 (10 mg) under 90 °C. (b) Pseudo-first-order fitting of total iodine adsorption at 90 °C by monitoring the absorption band at 292 nm, $k = (3.94 \pm 0.10) \times 10^{-3} \text{ s}^{-1}$.

[0044] Figure 35. Arrhenius-equation fitted data of total iodine adsorption ($E_a = 35.3 \pm 6.0 \text{ kJ/mol}$).

[0045] Figure 36. (a) time-dependent UV/Vis spectra of an I₂ aqueous solution (0.59 mM) in presence of HcOF-7 (10 mg). (b) Fitted pseudo-first-order plot for I₂ adsorption monitored at 460 nm, $k = (6.65 \pm 0.30) \times 10^{-4} \text{ s}^{-1}$.

[0046] Figure 37. (a) Time-dependent UV/Vis spectra of I₂/KI aqueous solution (0.59 mM I₂ + 0.59 mM KI) in presence of HcOF-7 (10 mg). (b) Fitted pseudo-first-order plot for iodine (I₂ and I₃⁻) adsorption monitored at 460 nm, $k = (6.11 \pm 0.23) \times 10^{-4} \text{ s}^{-1}$. (c) Fitted pseudo-first-order plot for iodine (I₂ and I₃⁻) monitored at 400 nm, $k = (6.20 \pm 0.12) \times 10^{-4} \text{ s}^{-1}$.

[0047] Figure 38. (a) Time-dependent UV/Vis spectra of I₂/KI aqueous solution (0.59 mM I₂ + 1.18 mM KI) in presence of HcOF-7 (10 mg). (b) Fitted pseudo-first-order plot for iodine (I₂ and I₃⁻) adsorption monitored at 460 nm, $k = (5.93 \pm 0.21) \times 10^{-4} \text{ s}^{-1}$. (c) Fitted pseudo-first-order plot for iodine (I₂ and I₃⁻) monitored at 400 nm, $k = (6.30 \pm 0.05) \times 10^{-4} \text{ s}^{-1}$.

[0048] Figure 39. (a) Time-dependent UV/Vis spectra of I₂/KI aqueous solution (0.59 mM I₂ + 7.08 mM KI) in presence of HcOF-7 (10 mg). (b) Fitted pseudo-first-order plot for iodine (I₂ and I₃⁻) adsorption monitored at 460 nm, $k = (2.97 \pm 0.06) \times 10^{-4} \text{ s}^{-1}$. (c) Fitted pseudo-first-order plot for iodine (I₂ and I₃⁻) adsorption monitored at 400 nm, $k = (2.93 \pm 0.06) \times 10^{-4} \text{ s}^{-1}$.

[0049] Figure 40. (a) UV/Vis spectra of I₂ aqueous solution (0.79 mM) before and after HcOF-7 (5 mg) addition using a 1 cm cuvette. (b-d) UV/Vis spectra of I₂/KI aqueous

solution (0.79 mM I₂, b: 1.58 mM KI, c: 3.95 mM KI, d: 9.48 mM KI) before and after HcOF-7 (5 mg) addition using a 0.1 cm cuvette.

[0050] Figure 41. UV/Vis spectra of 3.5 mM KI solutions before and after I⁻ exchange in the presence of HcOF-7 (5 mg). The solutions were diluted 50 times before the measurements.

[0051] Figure 42. I⁻ exchange amount for HcOF-7 (5 mg) in 3.5 mM KI solutions at 23 °C, 50 °C, and 90 °C.

[0052] Figure 43. FT-IR spectra of (a) HcOF-7, (b) HcOF-7 after I₂/KI adsorption, (c) HcOF-7 after I₂/KI removal and deprotonation, and (d) HcOF-7 after HNO₃ re-protonation.

[0053] Figure 44. PXRD profiles of (a) HcOF-7, (b) HcOF-7 after I₂/KI adsorption, and (c) HcOF-7 after I₂/KI removal and HNO₃ re-protonation.

[0054] Figure 45. UV/Vis spectra of 0.1, 0.2 and 0.3 g/L of I₂ solution (5 mL) before and after HcOF-7 (5mg) adsorption.

[0055] Figure 46. UV/Vis spectra of the 3.5 mM KI solution before and after adsorbing by HcOF-7, I₂•HcOF-7 (0.1 g/g), I₂•HcOF-7 (0.2 g/g), I₂•HcOF-7 (0.3 g/g) at 23 °C. The samples were diluted 50 times before the measurement.

[0056] Figure 47. Raman spectra of (a) HcOF-7, (b) HcOF-7 after soaking in I₂/KI solution (I₂: 0.87 M, KI: 1.02 M, 3 mL) for 72 h, and (c) HcOF-7 after exposed to I₂ vapor (45 °C) for 72 h.

[0057] Figure 48. PXRD profiles of as-synthesized HcOF, HcOF-7 after ball milling, and HcOF-7 after the (3.5 ppm I₂ + 1.5 ppm I⁻) breakthrough experiment and after I⁻ (3.5 mM) exchange.

[0058] Figure 49. Red: the total residual iodine [I₂ + I⁻] concentrations after the adsorption of HcOF-7 (6 mg) from a mixture of I₂/KI aqueous solutions (3.5 mg/L I₂ + 1.5 mg/L I⁻) at different temperatures. Blue: the total residual iodine [I₂ + I⁻] concentrations after the adsorption of HcOF-7 (6 mg) from KI aqueous solutions (1.5 mg/L I⁻) at different temperatures. Black: the total residual iodine [I₂ + I⁻] concentrations after adsorption of CHOP-7 (10 mg) from a mixture of I₂/KI aqueous solutions (3.5 mg/L I₂ + 1.5 mg/L I⁻) at different temperatures.

[0059] Figure 50. ¹H NMR spectra (500 MHz, DMSO-*d*₆) of compound **2** (17.2 mM, 0.5 mL DMSO-*d*₆) titrated with a DMSO-*d*₆ solution of iodine (0.858 M). From bottom to top: **2** only, **2** + 14.0 equivalents of iodine.

[0060] **Figure 51.** ^1H NMR spectra (500 MHz, $\text{CD}_3\text{CN}/\text{DMSO-}d_6$ 4:1) of compound **2** (8.6 mM, 0.4 mL CD_3CN + 0.1 mL $\text{DMSO-}d_6$) compound $\mathbf{2}\cdot 4\text{H}^+\cdot 4\text{NO}_3^-$ (8.6 mM, 0.4 mL CD_3CN + 0.1 mL $\text{DMSO-}d_6$).

[0061] **Figure 52.** ^1H NMR spectra (500 MHz, $\text{CD}_3\text{CN}/\text{DMSO-}d_6$ 4:1) of compound $\mathbf{2}\cdot 4\text{H}^+\cdot 4\text{NO}_3^-$ (8.6 mM, 0.4 mL CD_3CN + 0.1 mL $\text{DMSO-}d_6$) titrated with a $\text{DMSO-}d_6$ solution of iodine (0.429 M). From bottom to top: **2** only, **2** + 18.0 equivalents of iodine.

[0062] **Figure 53.** Measured concentrations of total residual iodine (input: 5 ppm of I_2 + I^-) before and after static adsorption using HcOF-7 (6 mg) in deionized (DI) water in the presence of NO_3^- (5 ppm), H_2PO_4^- (5 ppm), SO_4^{2-} (20 ppm), Cl^- (80 ppm), HCO_3^- (60 ppm), and their mixture.

[0063] **Figure 54.** Image of iodine solution (35 mg/L I_2 + 15 mg/L I^-) before and after through HcOF-7 column.

[0064] **Figure 55.** Images of HcOF-7 column before and after the iodine residue removal breakthrough experiment.

[0065] **Figure 56.** The total residual iodine (I_2 + I^-) concentration of a used I_2/I^- · HcOF-7 column upon 1L of tap water passing through at 23 °C. flow speed: 5 mL/min.

[0066] **Figure 57.** ^1H NMR spectrum of **S1** in $\text{DMSO-}d_6$ (500 MHz) recorded at 298 K.

[0067] **Figure 58.** ^{13}C NMR spectrum of **S1** in $\text{DMSO-}d_6$ (150 MHz) recorded at 298 K.

[0068] **Figure 59.** ^1H NMR spectrum of **S2** in $\text{DMSO-}d_6$ (500 MHz) recorded at 298 K.

[0069] **Figure 60.** ^{13}C NMR spectrum of **S2** in $\text{DMSO-}d_6$ (150 MHz) recorded at 298 K.

[0070] **Figure 61.** ESI-HRMS spectrum of **S2**.

[0071] **Figure 62.** ^1H NMR spectrum of **S3** in $\text{DMSO-}d_6$ (500 MHz) recorded at 298 K.

[0072] **Figure 63.** ^{13}C NMR spectrum of **S3** in $\text{DMSO-}d_6$ (150 MHz) recorded at 298 K.

[0073] **Figure 64.** ESI-HRMS spectrum of **S3**.

[0074] **Figure 65.** ^1H NMR spectrum of **1** in $\text{DMSO-}d_6$ (500 MHz) recorded at 298 K.

[0075] **Figure 66.** ^{13}C NMR spectrum of **1** in $\text{DMSO-}d_6$ (150 MHz) recorded at 298 K.

[0076] **Figure 67.** ESI-HRMS spectrum of **1**.

[0077] **Figure 68.** ^1H NMR spectrum of $\mathbf{1} \cdot 4\text{H}^+ \cdot 4\text{NO}_3^-$ crystal in $\text{DMSO-}d_6$ (500 MHz) recorded at 298 K.

[0078] **Figure 69.** ^{13}C NMR spectrum of $\mathbf{1} \cdot 4\text{H}^+ \cdot 4\text{NO}_3^-$ crystal in $\text{DMSO-}d_6$ (150 MHz) recorded at 298 K.

[0079] **Figure 70.** ^1H NMR spectrum of **2** in $\text{DMSO-}d_6$ (500 MHz) recorded at 298 K.

[0080] **Figure 71.** ^1H - ^{13}C HSQC NMR spectrum (500 MHz, $\text{DMSO-}d_6$) of **1** recorded at 298 K.

[0081] **Figure 72.** A schematic representation of iodine disinfection and residual iodine removal using ionic HcOF-7.

[0082] **Figure 73.** Iodine uptake amount for HcOF-7, activated carbon and HcOP-7 at different temperatures. HcOP-7 is also referred to as “CHOP-7” herein.

[0083] **Figure 74.** The residual concentration of $[\text{I}_2 + \text{I}^-]$ after HcOF-7 adsorption from a mixture of (3.5 mg/L I_2 + 1.5 mg/L I^-) solution and 1.5 mg/L I^- aqueous solution at different temperatures.

[0084] **Figure 75.** The residual concentration of $[\text{I}_2 + \text{I}^-]$ after HcOF-7 and HcOP-7 adsorption from a mixture of (3.5 mg/L I_2 + 1.5 mg/L I^-) solution at different temperatures.

[0085] **Figure 76.** I^- uptake amount for HcOF-7 at different temperatures.

[0086] **Figure 77.** Iodine adsorption for HcOF-7 at different initial concentrations.

[0087] **Figure 78.** Langmuir model fitting of iodine adsorption for HcOF-7 ($q_{\text{max}} = 722.2 \text{ mg/g}$, $K = 4.19 \times 10^{-3} \text{ L/mg}$).

[0088] **Figure 79.** Raman spectrum of HcOF-7 after I_2 and I^- uptake.

[0089] **Figure 80.** The residual concentrations of total iodine ($\text{I}_2 + \text{I}^-$) in water after passing through the HcOF-7, activated carbon, and the mixture-bed columns measured using the Leuco-crystal violet method. Iodinated water ($\text{I}_2 + \text{KI}$, 3.5 + 1.5 ppm) was pumped into a customized steel precolumn (d: 50 × 1: 220 mm) and heated to the desired temperatures under continuous flow (5 mL/min).

DETAILED DESCRIPTION OF THE DISCLOSURE

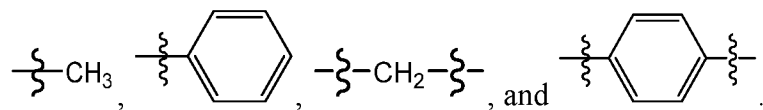
[0090] Although claimed subject matter will be described in terms of certain embodiments, other embodiments, including embodiments that do not provide all of the benefits and features set forth herein, are also within the scope of this disclosure. Various

structural, logical, and process step changes may be made without departing from the scope of the disclosure.

[0091] Ranges of values are disclosed herein. The ranges set out a lower limit value and an upper limit value. Unless otherwise stated, the ranges include all values to the magnitude of the smallest value (either lower limit value or upper limit value) and ranges between the values of the stated range.

[0092] As used herein, unless otherwise stated, the term “group” refers to a chemical entity that is monovalent (i.e., has one terminus that can be covalently bonded to other chemical species), divalent, or polyvalent (i.e., has two or more termini that can be covalently bonded to other chemical species). The term “group” also includes radicals (e.g., monovalent and multivalent, such as, for example, divalent radicals, trivalent radicals, and the like).

Illustrative examples of groups include:



[0093] As used herein, unless otherwise indicated, the term “aliphatic groups” refers to branched or unbranched hydrocarbon groups that, optionally, contain one or more degrees of unsaturation. Degrees of unsaturation include, but are not limited to, alkenyl groups, alkynyl groups, and aliphatic cyclic groups. Aliphatic groups may be a C₁ to C₂₀ aliphatic group, including all integer numbers of carbons and ranges of numbers of carbons therebetween (e.g., C₁, C₂, C₃, C₄, C₅, C₆, C₇, C₈, C₉, C₁₀, C₁₁, C₁₂, C₁₃, C₁₄, C₁₅, C₁₆, C₁₇, C₁₈, C₁₉, and C₂₀). Aliphatic groups may be unsubstituted or substituted with one or more substituents. Examples of substituents include, but are not limited to, heteroatoms (e.g., -O, -S, -N, -P), halogens (-F, -Cl, -Br, and -I), aliphatic groups (e.g., alkyl groups, alkenyl groups, alkynyl groups, and the like), halogenated aliphatic groups (e.g., trifluoromethyl group and the like), aryl groups, halogenated aryl groups, alkoxide groups, amine groups, nitro groups, carboxylate groups, carboxylic acids, ether groups, thioether or sulfide groups, alcohol groups, alkyne groups (e.g., acetylenyl groups and the like), and the like, and combinations thereof. Aliphatic groups may be alkyl groups, alkenyl groups, alkynyl groups, or carbocyclic groups, and the like.

[0094] As used herein, unless otherwise indicated, the term “alkyl group” refers to branched or unbranched saturated hydrocarbon groups. Examples of alkyl groups include, but are not limited to, methyl groups, ethyl groups, propyl groups, butyl groups, isopropyl groups, tert-butyl groups, and the like. For example, the alkyl group is C₁ to C₂₀, including all

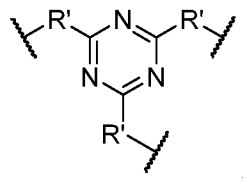
integer numbers of carbons and ranges of numbers of carbons therebetween (e.g., C₁, C₂, C₃, C₄, C₅, C₆, C₇, C₈, C₉, C₁₀, C₁₁, C₁₂, C₁₃, C₁₄, C₁₅, C₁₆, C₁₇, C₁₈, C₁₉, and C₂₀). The alkyl group may be unsubstituted or substituted with one or more substituents. Examples of substituents include, but are not limited to, various substituents such as, for example, halogens (-F, -Cl, -Br, and -I), aliphatic groups (e.g., alkyl groups, alkenyl groups, alkynyl groups, and the like), aryl groups, alkoxide groups, carboxylate groups, carboxylic acids, ether groups, amine groups, and the like, and combinations thereof.

[0095] The present disclosure provides organic frameworks. The organic frameworks comprise, consistent essentially of, or consist of a plurality of linked monomers. The monomers may be linked covalently and/or ionically. Also disclosed are articles comprising the organic frameworks, methods of making the organic frameworks, and methods of using the organic frameworks. The organic frameworks may be used to remove I₂ and I⁻ from a medium (e.g., water).

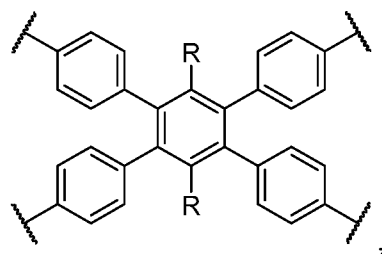
[0096] Iodine is widely used as an antimicrobial reagent for water disinfection in extreme environments (e.g., wild fields and outer space), but the residual iodine needs to be removed for health reasons. However, it is challenging to remove these residues due to the low concentration of iodine and iodides (~ 5 ppm), especially across a broad temperature range (up to 90 °C). This work provided the development of a single-crystalline ionic hydrogen-bonded crosslinked organic framework (HcOF-7), which was synthesized through a nitrate dimer-templated crystallization, followed by single-crystal to single-crystal crosslinking. HcOF-7 removes iodine and iodide species in water through halogen bonding interactions and anion exchange. Furthermore, the adsorbed iodine in HcOF-7 promotes the anion exchange, effectively reducing the total iodine residues from 5 to 0.22 ppm at room temperature. The packed HcOF-7 columns were employed for iodine breakthrough experiments between 23-90 °C, and large breakthrough volumes were recorded (20.3-18.3-L/g), respectively. These results provide design principles for a collective removal of neutral and anionic iodine residues in the aqueous environment at low concentrations. This work also sets up benchmarks using porous framework materials for drinking water disinfection and iodine removal for practical uses.

[0097] In an aspect, the present disclosure provides organic frameworks. The organic frameworks may be crystalline and be a plurality of single crystals. The organic frameworks have a hydrogen-bonded network that may help define the dimensions of the apertures defined by the monomeric units of the organic frameworks.

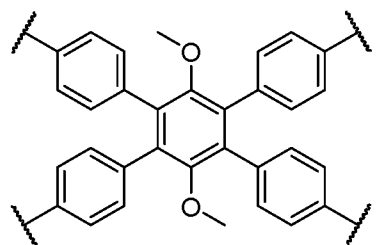
[0098] The organic frameworks may be made from various components/monomers. For example, a monomer may comprise a plurality of the following group:



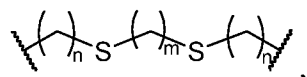
which may be referred to as “A groups,” where R’ is –NH– or –O–. One or more A groups may be covalently attached to:



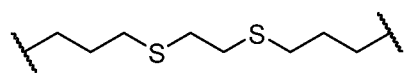
which may be referred to as “B groups,” where each R may individually be chosen from hydrogen, methoxy groups, ethoxy groups, alkoxy groups, alkylamino groups, alkyl ester groups, and alkyl groups. For example, the B groups may have the following structure:



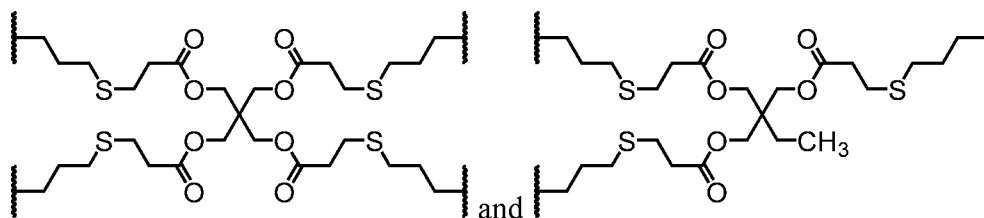
The A groups may further be covalently attached to one or more other A groups (which are attached to other B groups) via a crosslinking group and/or ionically bound via a counterion (e.g., NO₃[−]). The crosslinking group may have the following structure:



wherein n is 2 to 8 and m is 1 to 8. In various embodiments, the crosslinking groups have the following structure:



Other non-limiting examples of crosslinking groups include:



Each A group may be attached by one or two crosslinking groups to other A groups. The counterions may be exchanged with other counterions after covalent crosslinking.

[0099] In various embodiments, the A groups may be crosslinked by various ions. For example, the monomers are ionically crosslinked prior to covalent crosslinking. The ions may be anions. For example, the ions are NO_3^- groups. Other examples of anions include, but are not limited to, SO_4^{2-} , CO_3^{2-} , HSO_4^- , HCO_3^- , H_2PO_4^- , HPO_4^{2-} , PO_4^{3-} , Cl^- , F^- , and Br^- . These ions may be replaced or exchanged following covalent crosslinking. For example, ions (e.g., nitrate ions) may be replaced with I_2 and/or I^- following covalent crosslinking.

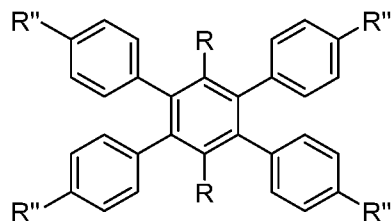
[0100] The orientation of the monomers in the organic framework defines one or more apertures. The apertures may have various dimensions (e.g., a longest linear dimension, such as, for example, a diameter). The apertures may or may not be uniformly shaped. For example, each aperture may have a longest linear dimension may be 3–15 Å, including all 0.1 Å values and ranges therebetween (e.g., 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, or 15 Å). In various embodiments, one or more of the apertures have are about 6 Å x 12 Å. Ions may be in the void of the aperture. The size of the aperture may be controlled during crystallization of the monomers. For example, crystallization with different solvents will result in different sized apertures. Different ions may affect the size of the aperture.

[0101] The organic framework may be crystalline. The crystals may be single crystals. The crystal system may be a triclinic crystal system. It may have a *P-1* space group. In other embodiments, the crystal system may be a monoclinic crystal system and have a *P2₁/c* space group. The crystal system and space group is determined by the solvent used during crystallization. In various embodiments, the organic frameworks of the present disclosure do not comprise amorphous domains. In various embodiments, the organic frameworks are at least 90% (e.g., 90%, 91%, 92%, 93%, 94%, 95%, 96%, 97%, 98% and 99%). In various embodiments, the organic frameworks are greater than 99% crystalline. In other embodiments, such as, for example, CHOP-7 embodiments, the organic frameworks may be up to 100% amorphous, or they may be 100% amorphous.

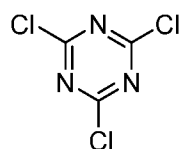
[0102] In an aspect, the present disclosure provides methods of making organic frameworks of the present disclosure. The methods for making the organic frameworks are described herein.

[0103] In various embodiments, a method for making an organic framework

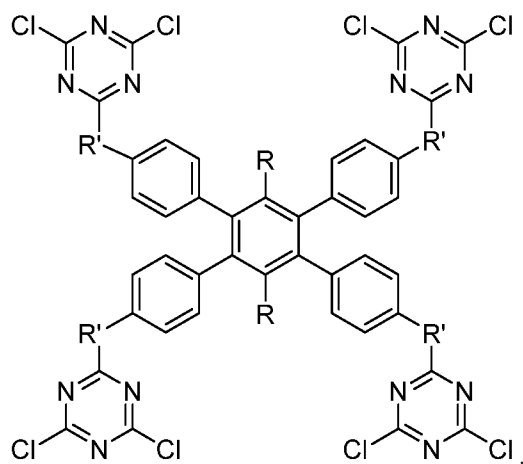
5 comprises reacting



with



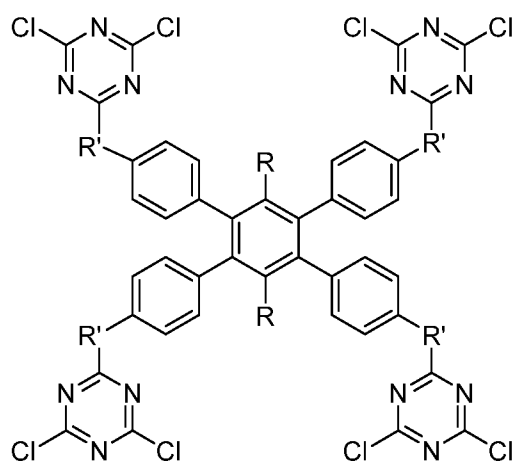
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The reaction may be performed under basic conditions (e.g., a reaction mixture comprising K_2CO_3 in THF at 0 °C). R may be individually chosen from hydrogen, methoxy groups, ethoxy groups, alkoxy groups, alkylamino groups, alkyl ester groups, and alkyl groups. Each R' may independently be $-NH-$ or $-O-$. Each R'' may independently be $-NH_2$ and $-OH$. The

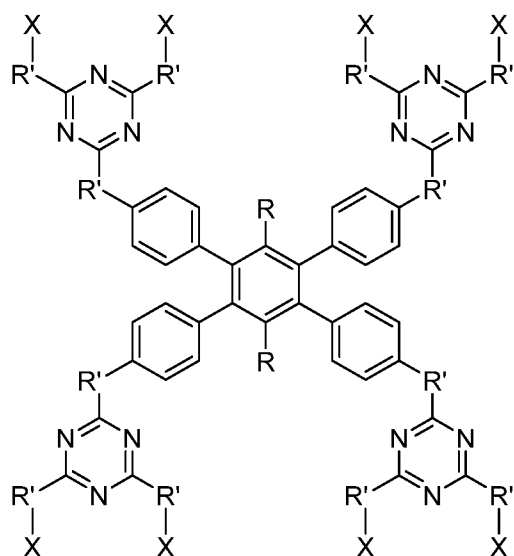
15 method further comprises reacting



with

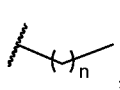
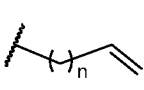
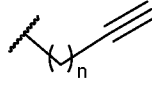
$R''-X$

to form

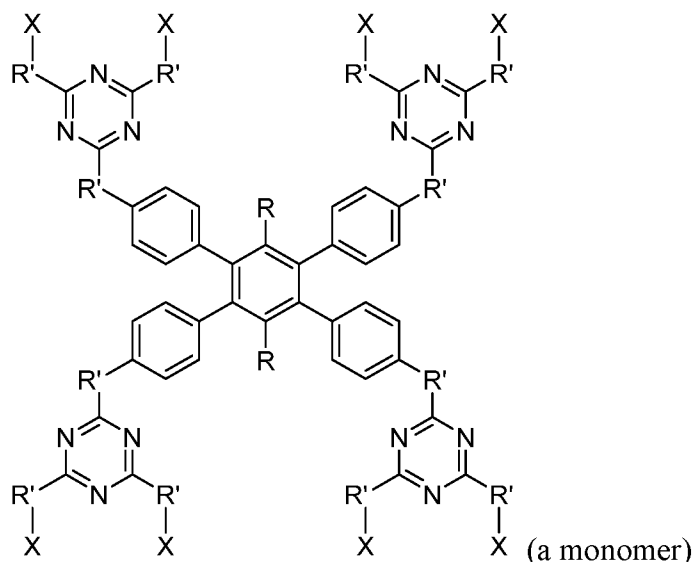


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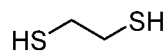
R'' may independently be $-NH_2$ or $-OH$, and each X is an aliphatic group. For example, X

may be chosen from , , and , where n is 1, 2, or 3. The reaction may be performed under basic conditions (e.g., a reaction mixture comprising

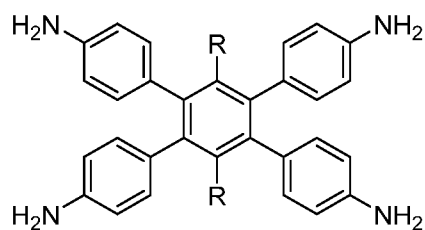
DIPEA at 120 °C). The method further comprises contacting



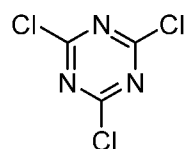
with a solvent to generate complexation of ions and/or solvent groups to the monomers. For example, the monomer is contacted with an acid (e.g., nitric acid) such that the resulting conjugate base ions (e.g., nitrate ions) are complexed to the monomers. The monomers may then be ionically crosslinked. Following by this, the ionically crosslinked monomers are covalently crosslinked by contacting with a linking group, such as, for example,



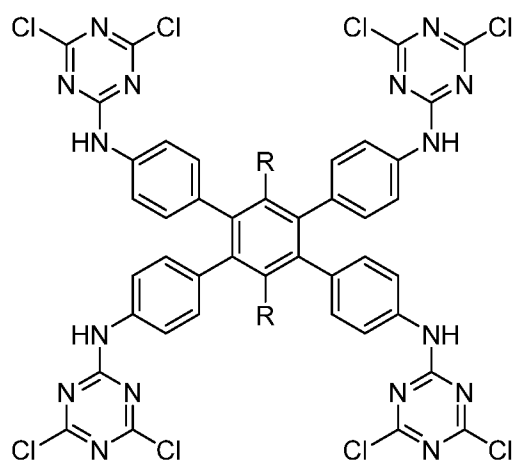
[0104] In some embodiments, for example, the method for making an organic framework comprises reacting



with

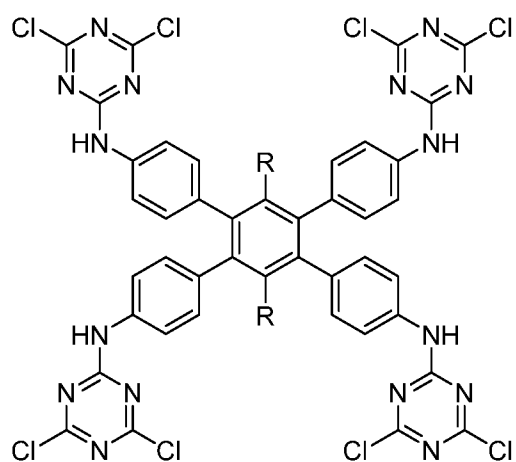


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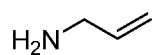


The reaction may be performed under basic conditions (e.g., a reaction mixture comprising K_2CO_3 in THF at 0 °C). R may be individually chosen from hydrogen, methoxy groups, ethoxy groups, alkoxy groups, alkylamino groups, alkyl ester groups, and alkyl groups. The

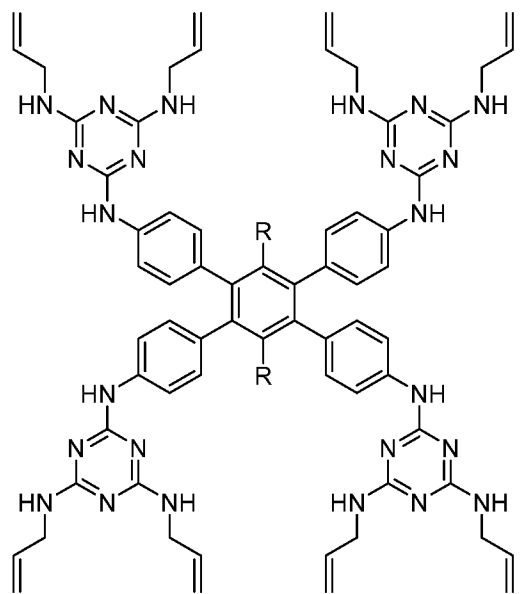
5 method further comprises reacting



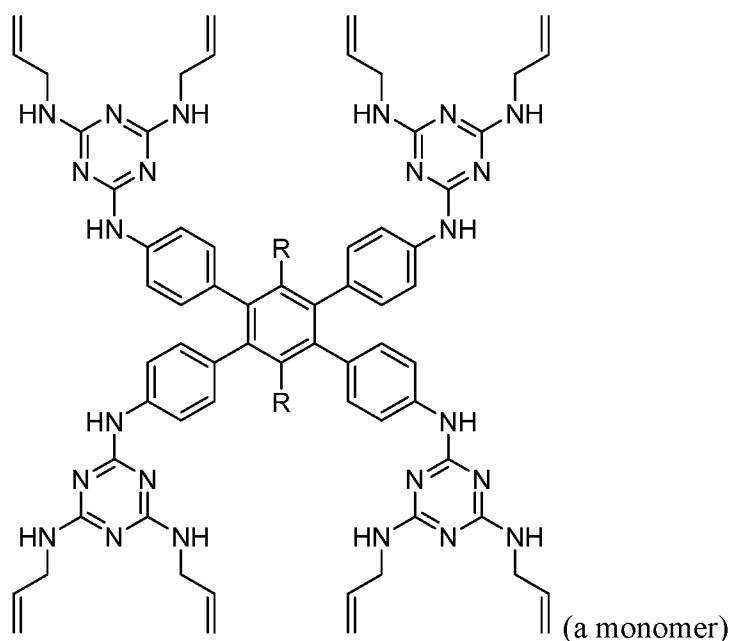
with



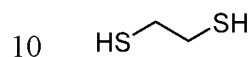
to form



The reaction may be performed under basic conditions (e.g., a reaction mixture comprising DIPEA at 120 °C). The method further comprises contacting



- 5 with a solvent to generate complexation of ions and/or solvent groups to the monomers. For example, the monomer is contacted with an acid (e.g., nitric acid) such that the resulting conjugate base ions (e.g., nitrate ions) are complexed to the monomers. The monomers may then be ionically crosslinked. Following by this, the ionically crosslinked monomers are covalently crosslinked by contacting with a linking group, such as, for example,

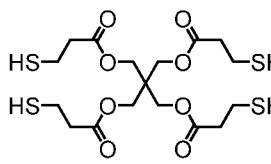
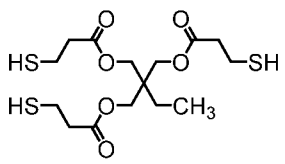


The resulting organic framework is depicted in Figure 3a and 6.

[0105] Various acids may be used in a method of preparing an organic framework of the present disclosure. Examples of acids include, but are not limited to, H_2SO_4 , H_2CO_3 , H_2SO_4 , H_3PO_4 , HNO_3 , HCl , HF , and HBr .

[0106] Various crosslinkers may be used in a method of making an organic

5 framework of the present disclosure. Examples of crosslinkers include, but are not limited to,

propane dithiol, butanedithiol, $\text{HS}-\text{CH}_2-\text{CH}_2-\text{SH}$, , and .

[0107] In an aspect, the present disclosure provides articles of manufacture. The article of manufacture comprises one or more organic frameworks of the present disclosure. The article of manufacture may be referred to as an article. The article may be a filtration
10 funnel, a centrifuge tube, a chromatography column, a vessel, a reaction vessel, a filtration cartridge, a filtration membrane, a fritted funnel, a syringe, or the like.

[0108] In an aspect, the present disclosure provides a method for removing iodine (e.g., I_2 , I^- , and/or I_3^-) from an aqueous medium, such as, for example, from water.

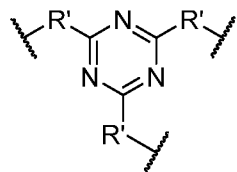
[0109] The method may comprise contacting water with an organic framework of the
15 present disclosure. The organic framework may be a plurality of single crystals. The water may be contacted with an article comprising the organic framework. The organic framework may be disposed on a surface of the organic framework. The contacting may be done at a temperature greater than room temperature (e.g., 40°C or greater, 50°C or greater, 60°C or greater, 70°C or greater, 80°C or greater, 85°C or greater, or at least 90°C). Following
20 contact with the organic frameworks of the present disclosure, the potability of the contacted water is expected to increase.

[0110] In various embodiments, the organic frameworks of the present disclosure may be used to capture or exchange radioactive iodine. For example, radioactive iodine may be released into water and/or soil as I_2 or I^- . The contaminated matter (e.g., soil, water, and/or
25 the like) may be contacted with an organic framework or article of the present disclosure.

[0111] The steps of the method described in the various embodiments and examples disclosed herein are sufficient to carry out the methods of the present invention. Thus, in an embodiment, the method consists essentially of a combination of the steps of the methods disclosed herein. In another embodiment, the method consists of such steps.

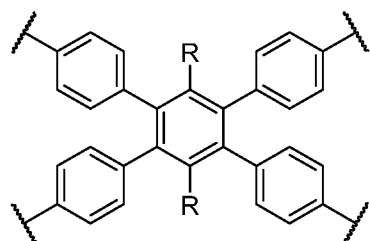
30 **[0112]** The following Statements provide various embodiments of the present disclosure.

Statement 1. An organic framework comprising a plurality of linked monomers comprising one or more



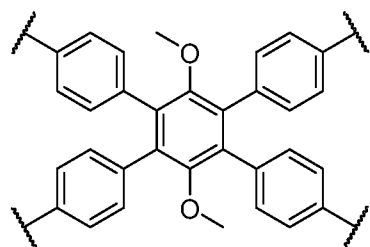
(“A group”) and the organic framework is at least 95% (e.g., 95%, 96%, 97%, 98%, 99%, or
5 100%) crystalline.

Statement 2. An organic framework according to Statement 1, wherein the monomers further comprise:

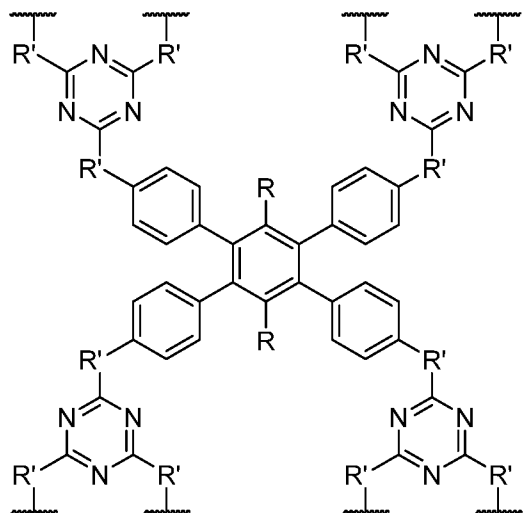


10 (“B group”), wherein each R is individually chosen from hydrogen, methoxy groups, ethoxy groups, alkoxy groups, alkylamino groups, alkyl ester groups, and alkyl groups; and each B group is covalently bonded to one or more A group.

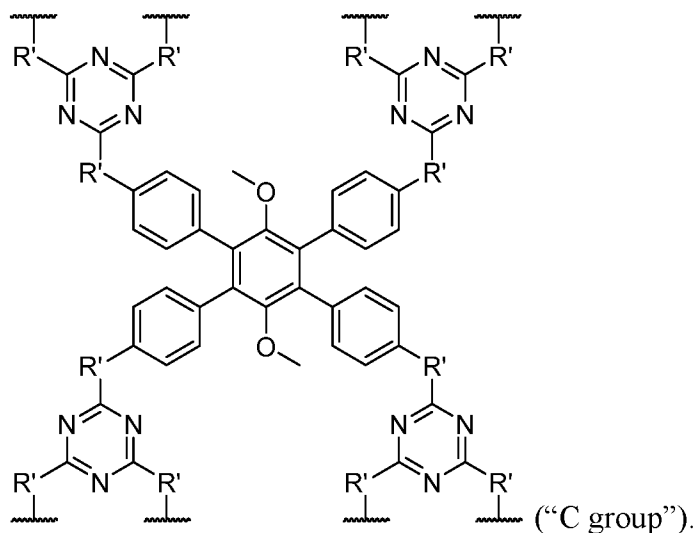
Statement 3. An organic framework according to Statements 1 or 2, wherein the B group has
15 the following structure:



Statement 4. An organic framework according to Statement 3, comprising (e.g., wherein the monomer has the following structure):

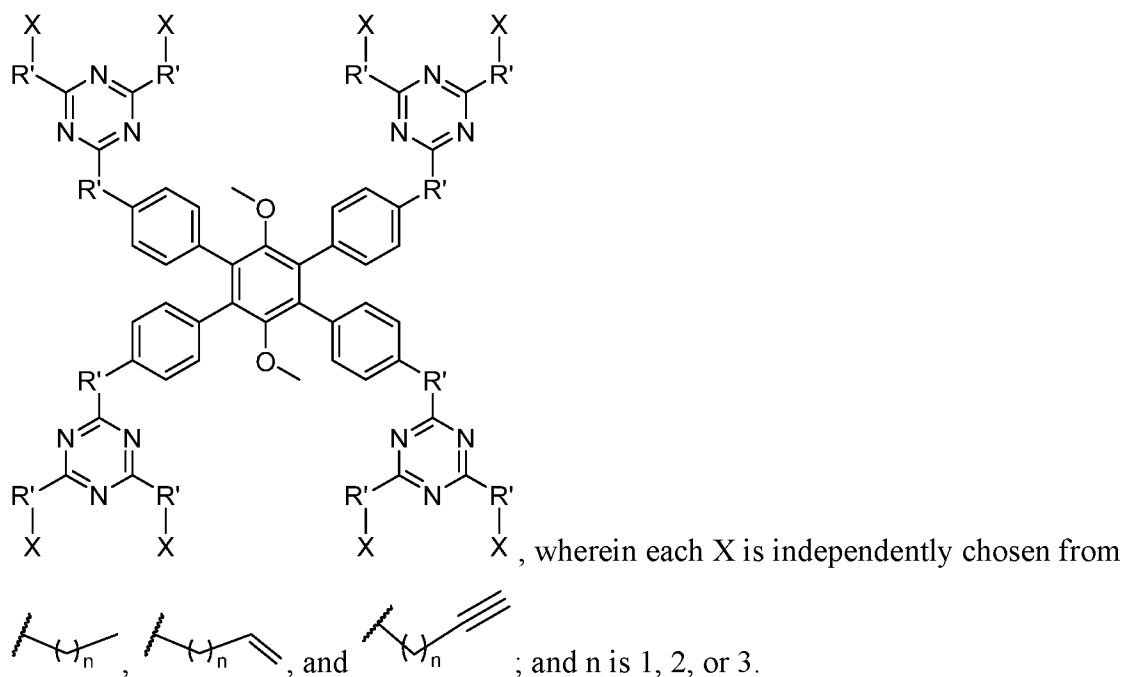


- 5 Statement 5. An organic framework according to Statement 4, comprising (e.g., wherein the monomer has the following structure):



- Statement 6. An organic framework according to Statement 5, wherein one or more C groups
10 are connected to other C groups via a crosslinking group.

Statement 7. An organic framework according to Statement 5, comprising (e.g., wherein monomer has the following structure):

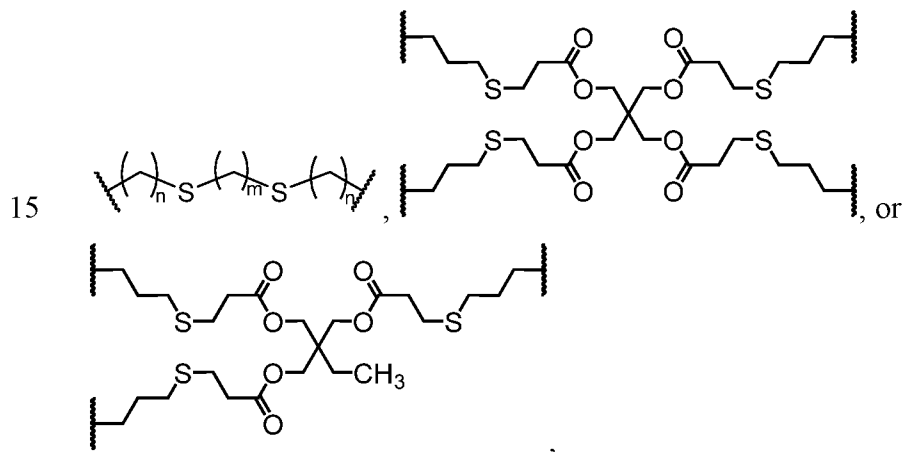


Statement 8. An organic framework according to Statement 7, wherein the monomers are crosslinked via NO_3^- ions.

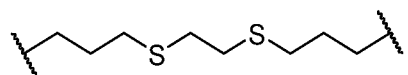
Statement 9. An organic framework according to Statement 6, wherein the crosslinked C groups have NO_3^- bound thereto.

Statement 10. An organic framework according to Statement 6, wherein the crosslinked C groups have I_2 and/or I^- and/or I_3^- bound thereto.

Statement 11. An organic framework according to Statement 6, wherein the crosslinking group has the following structure:



Statement 12. An organic framework according to Statement 11, wherein the crosslinking group has the following structure:



5

Statement 13. An organic framework according to any one of the preceding Statements, wherein the organic framework defines one or more apertures.

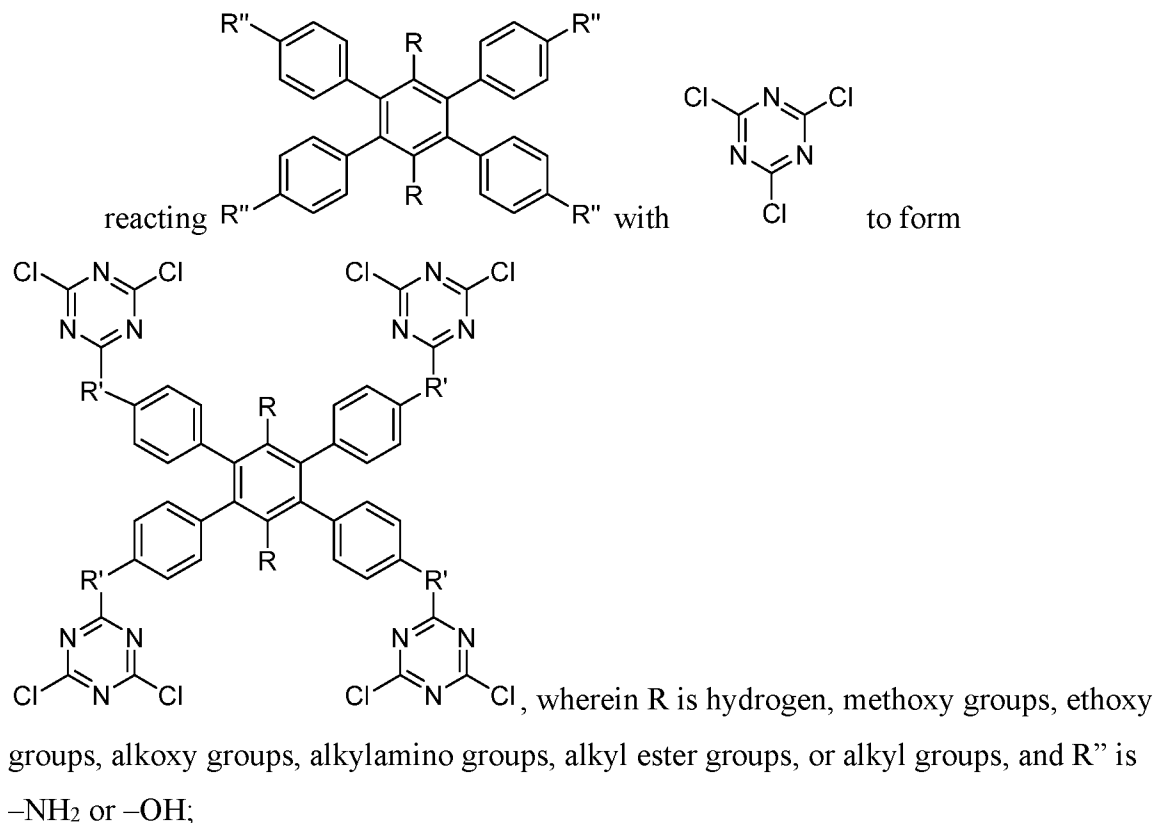
Statement 14. An organic framework according to Statement 13, wherein the aperture has a longest linear dimension of 3–15 Å, including all 0.1 Å values and ranges therebetween (e.g., 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, or 15 Å).

10

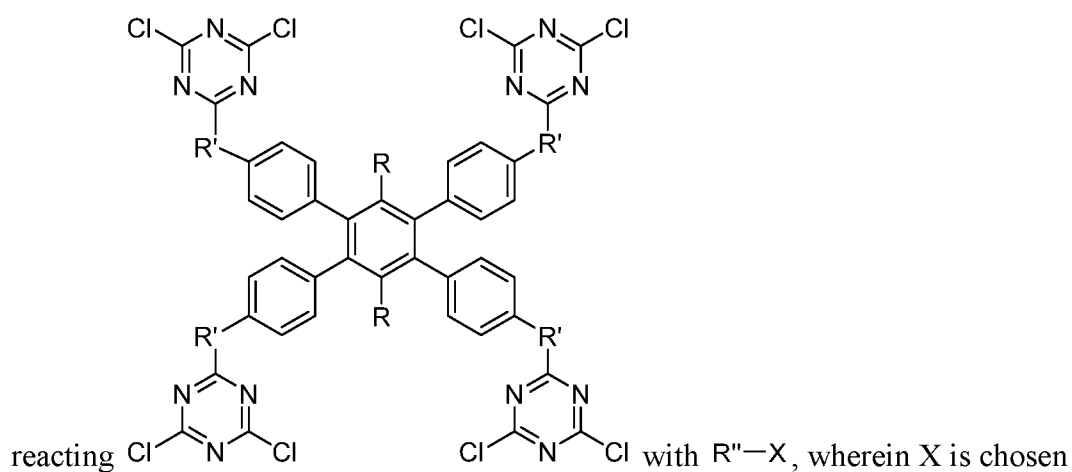
Statement 15. An organic framework according to Statement 13, wherein the aperture is about or is 6 Å x 12 Å.

15

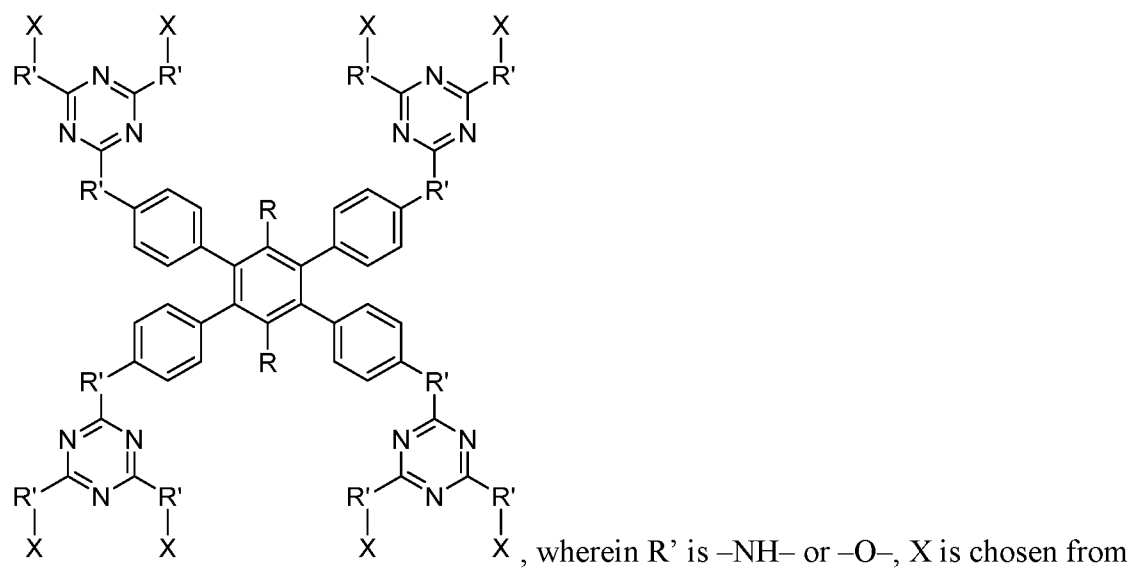
Statement 16. An organic framework made by a process comprising:



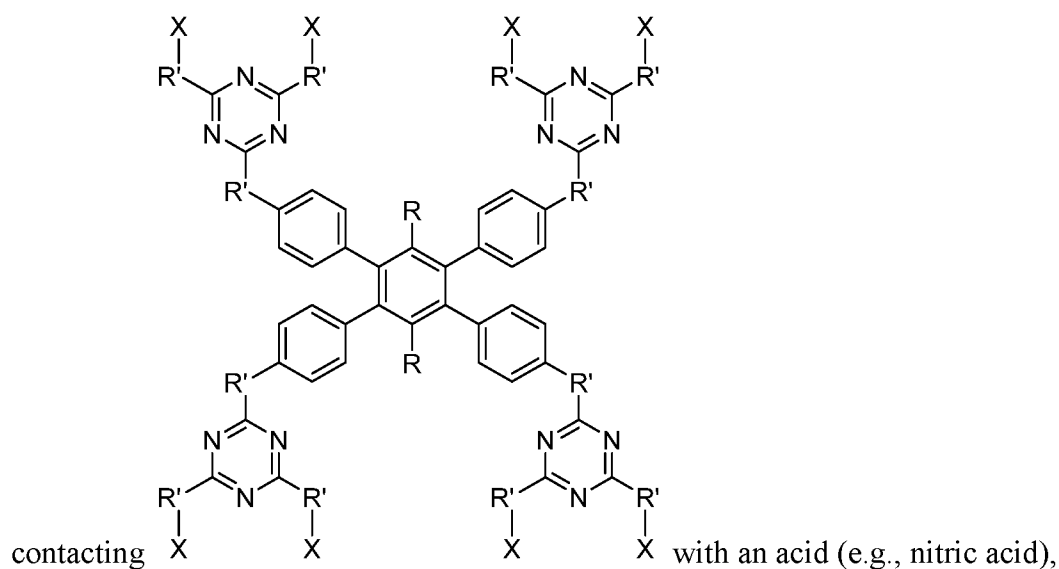
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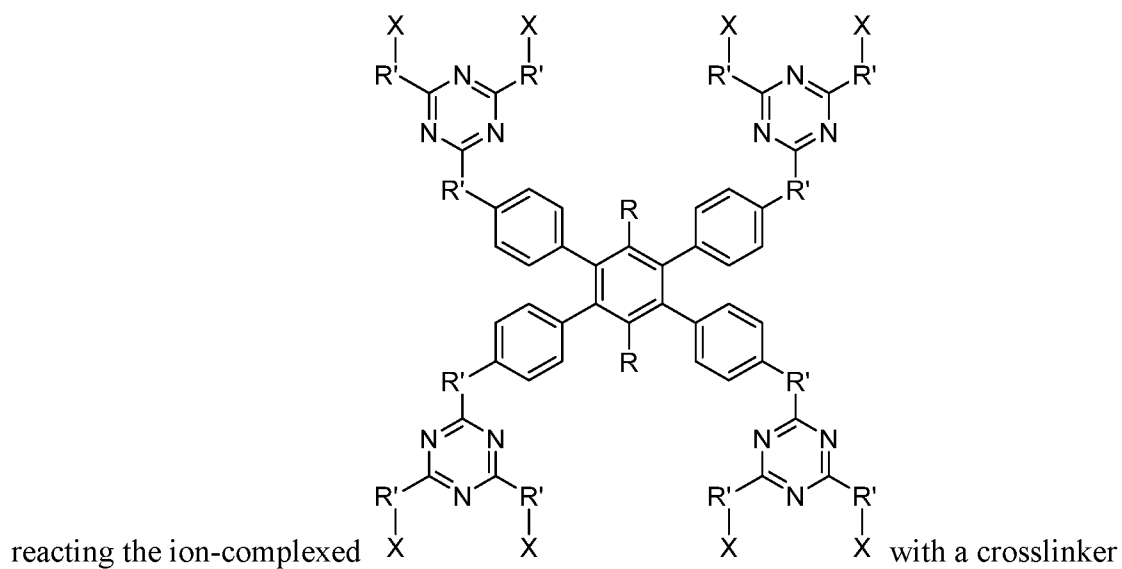
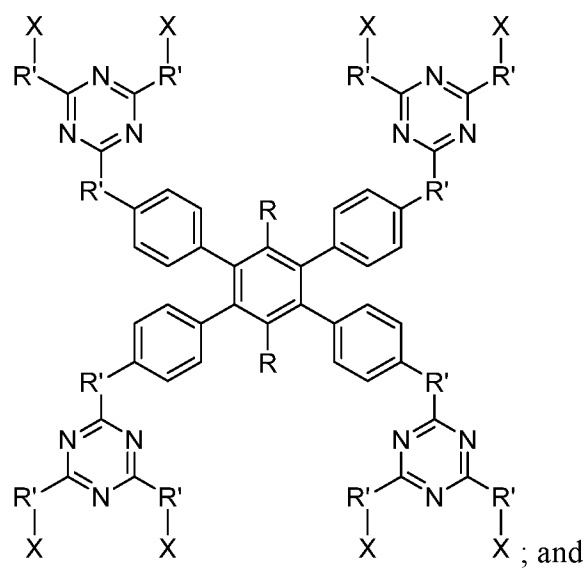
from $\text{---}(\text{---})_n\text{---}$, $\text{---}(\text{---})_n\text{---CH=CH}_2$, and $\text{---}(\text{---})_n\text{---C}\equiv\text{C}_2$; and n is 1, 2, or 3, to form



5 $\text{---}(\text{---})_n\text{---}$, $\text{---}(\text{---})_n\text{---CH=CH}_2$, and $\text{---}(\text{---})_n\text{---C}\equiv\text{C}_2$; and n is 1, 2, or 3;



such that conjugate base ions of the acid (e.g., nitrate ions) complex to



5 (e.g., HS—CH₂—CH₂—SH), wherein a crosslinked organic framework is formed.

Statement 17. An organic framework according to Statement 16, wherein the acid is H_2SO_4 , H_2CO_3 , H_2SO_4 , H_3PO_4 , HNO_3 , HCl , HF , or HBr .

- 5 Statement 18. An organic framework according to Statement 16 or Statement 17, wherein R is a methoxy group.

Statement 19. An article of manufacture comprising an organic framework according to any one of the preceding Statements.

10

Statement 20. An article of manufacture according to Statement 19, wherein the article is a vessel, a column, a centrifuge tube, a filter, a fritted funnel, a syringe, or a filtration membrane.

- 15 Statement 21. A method for removing I_2 and/or I^- comprising contacting a medium comprising I_2 and/or I^- with an organic framework according to any one of Statements 1–18.

Statement 22. A method according to Statement 21, wherein the medium is water.

- 20 Statement 23. A method according to Statement 21 or Statement 22, wherein the organic framework is a plurality of single crystals.

Statement 24. A method according to any one of Statements 21–23, wherein an article comprises or has disposed on a surface thereof the organic framework.

25

Statement 25. A method according to any one of Statements 21–2, wherein the contacting is performed at a temperature greater than room temperature.

- 30 Statement 26. A method according to any one of Statements 21–25, wherein the temperature is 40°C or greater.

Statement 27. A method according to any one of Statements 21–26, wherein the temperature is 50°C or greater.

Statement 28. The method according to any one of Statements 21–27, wherein the temperature is 85 °C or greater.

Statement 29. A method according to any one of Statements 21–28, wherein the temperature is at least 90 °C.

[0113] The following example is presented to illustrate the present disclosure. It is not intended to be limiting in any matter.

EXAMPLE 1

10 [0114] This example provides a description of organic frameworks of the present disclosure and methods of making and using same.

[0115] Monomer **1** was designed with a 1,2,4,5-tetraphenylbenzene core to increase the steric barrier for the four surrounding phenyl groups, forcing them to rotate perpendicularly to the center dimethoxy-benzene moiety to prevent π - π stacking in the solid-state (Figure 2a). Monomer **1** was synthesized in four steps in a high yield without column chromatography purification (Scheme 1). Single crystals of **1** were obtained by diffusing methanol into the DMSO solution of **1** at room temperature for 5 days. Single-crystal X-ray diffraction (SCXRD) analysis (Figure 2b-c) showed that **1** crystallized in a monoclinic $P2_1/n$ space group ($a = 15.0148$, $b = 14.7706$, $c = 16.4854$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 103.120^\circ$). The 15 dihedral angles between the four phenyl rings and the center dimethoxy-benzene moiety are measured between 53° and 63° (Figure 2b), which are larger than those in the tetraphenylethylene core of prior HcOFs. In the solid state, each monomer forms 16 intermolecular hydrogen bonds ($N\cdots NH$ distances: 2.99–3.09 Å) with the neighboring monomers, affording a hydrogen-bonded network (Figure 2c) of *pcu* topology (Figure 6). 20 **1**_{crystal} possesses 11% isolated voids occupied by disordered solvents (Figure 7).

[0116] Protonation of the melamine groups of **1** using nitric acid afforded **1**•4H⁺•4NO₃⁻, and the proton resonance of the melaminium NH was found at 10.3 ppm in the ¹H NMR spectrum (Figure 8). Thermogravimetric analysis (TGA) showed a mass loss of 17% at around 160 °C, attributed to nitrate loss in **1**•4H⁺•4NO₃⁻ (Figure 9). Single crystals of 30 **1**•4H⁺•4NO₃⁻ were obtained by crystallizing **1** in the presence of nitric acid (Figure 2d). **1**•4H⁺•4NO₃⁻_{crystal} crystallized in a triclinic $P\bar{1}$ space group (Figure 2e-i, $a = 10.3457$, $b = 15.3155$, $c = 16.9364$ Å, $\alpha = 77.121^\circ$, $\beta = 77.174^\circ$, $\gamma = 81.156^\circ$). Each melaminium moiety of

$1 \cdot 4\text{H}^+ \cdot 4\text{NO}_3^-$ acts as a hydrogen-bonding donor, which binds two anionic nitrates with $\text{O} \cdots \text{HN}$ hydrogen bonds ranging between 2.78 to 2.94 Å. The nitrate anion dimer is only 3.27 Å apart ($\text{N} \cdots \text{N}$ distance, Figure 2g), which measures the shortest nitrate-to-nitrate distance in solid-state assemblies, thus suggesting a large Coulombic repulsion between the two nitrates.

The donor-donor-donor (DDD) and acceptor-acceptor-acceptor (AAA) arrays formed between melaminiums and nitrate dimer are non-planar with an angle of 111.3° . One nitrate is further stabilized by two additional side-on Ph-NH -melaminium and NH-allyl hydrogen bonds (Figure 2g, yellow and green colored moieties), forming a third DD-AA array. This observation, in conjunction with other reported nitrate dimer assemblies, suggests that the nitrate-melamine assembly is sensitive to the molecular geometry of the melamine-containing molecule and its solid structure. Compared to HCO_3^- , H_2PO_4^- or HSO_4^- anion dimers/clusters, the lack of hydrogen bonds between the two nitrates makes them less stable and directional in organizing the hydrogen-bonded networks. Consequently, the nitrate dimers should be more active in anion exchange to reduce their Coulombic repulsion. $1 \cdot 4\text{H}^+ \cdot 4\text{NO}_3^-$ crystal has limited stability since it lost crystallinity when exposed to diethylether, ethylacetate, or open-air (Figure 10). It also dissolves in dichloromethane, acetone, acetonitrile, and methanol.

[0117] The nitrate dimer may be a four-connected linker and $1 \cdot 4\text{H}^+$ may be a six-connected node for the construction of the hydrogen-bonded network. The topology of $1 \cdot 4\text{H}^+ \cdot 4\text{NO}_3^-$ crystal is assigned as a 3D network $\{4^{12}.6^{12}.8^4\}_2$ of *flu* topology (Figure 2h). The void space of $1 \cdot 4\text{H}^+ \cdot 4\text{NO}_3^-$ crystal is calculated as 35% (Figure 2i), filled by 1,4-dioxanes. There are interconnected 1D channels along the *a*-, *b*-, and *c*-axis, and their aperture sizes are measured as 3.9×19.4 , 6.8×7.6 , and 4.6×5.9 Å, respectively. The olefin groups of the diallyl-melaminium moieties are decorated on the accessible pore surface with various distances between 5 to 9 Å (Figure 12 and Table 2), which are suitable for crosslinking using 1,2-ethanedithiol (EDT).

[0118] It was discovered that EDT could not replace the 1,4-dioxanes in the voids of $1 \cdot 4\text{H}^+ \cdot 4\text{NO}_3^-$ crystal. Hence, the 1,4-dioxane molecules in $1 \cdot 4\text{H}^+ \cdot 4\text{NO}_3^-$ crystal were first replaced by THF (Figure 15) without diminishing the crystallinity. The THF-filled single crystals of $1 \cdot 4\text{H}^+ \cdot 4\text{NO}_3^-$ were immersed in a cyclohexane solution of EDT (133.2 μL/mL) for 3 d in the dark (Figure 16). After UV irradiation, the crosslinked samples were subjected to ^1H NMR and elemental analyses (Figure 17 and Table 3). Gradually increasing the concentration of EDT from 33.3 to 133.2 μL/mL, a close-to-stoichiometrically crosslinked HcOF-7 was obtained ($1 \cdot 4\text{H}^+ \cdot [\text{NO}_3^-]_{4.0} \cdot [\text{EDT}]_{3.95}$). In the FT-IR spectra (Figure 3b), the olefin bending band at 915 cm^{-1} disappeared after crosslinking. Only trace thiol stretching band was found at

2600 cm^{-1} in the Raman spectrum (Figure 3c). In the solid-state ^{13}C NMR spectrum (Figure 3d), new carbon resonances at 30.1 ppm attributed to the dithioether were observed, and resonances attributed to the olefins (115 and 131 ppm) disappeared after crosslinking, indicating the complete allyl-to-thioether conversion. HcOF-7 showed a nearly identical powder X-ray diffraction (PXRD) profile compared to that of $1\cdot 4\text{H}^+\cdot 4\text{NO}_3^-$ crystal (Figure 3e). In contrast to $1\cdot 4\text{H}^+\cdot 4\text{NO}_3^-$ crystal, HcOF-7 remained highly crystalline when exposed to water, dichloromethane, acetonitrile, acetone, open-air, and vacuum (Figure 18). The greatly improved chemical stability of HcOF-7 comes from the covalent thioether linkages.

[0119] HcOF-7 is suitable for SCXRD analysis (Figure 4a), and its cell volume expanded by 7.3 % compared to that of $1\cdot 4\text{H}^+\cdot 4\text{NO}_3^-$ crystal. The hydrogen-bonded network of HcOF-7 remained largely identical to $1\cdot 4\text{H}^+\cdot 4\text{NO}_3^-$ crystal. Analysis of the overlaid structure (Figure 4b) of $1\cdot 4\text{H}^+\cdot 4\text{NO}_3^-$ crystal and HcOF-7 showed that the $\text{O}\cdots\text{NH}$ hydrogen bonding distances between melaminium and nitrate dimers increased from 2.78 to 2.88 Å after crosslinking. The distance between the nitrates in the anion dimer increased from 3.27 to 3.48 Å. The larger hydrogen bond lengths and nitrate-nitrate distances suggest weaker hydrogen bonding interactions between the melaminiums and nitrate dimers in HcOF-7, thus making anion exchange more favorable.

[0120] In the refined solid-state structure of HcOF-7 (Figure 4c), each $1\cdot 4\text{H}^+$ moiety is connected to four neighboring moieties via dithioether crosslinks. Electron densities attributed to the dithioether crosslinkages indicate the co-existence of several crosslinking paths (Figure 20). The dithioether may be considered a two-connected linker and $1\cdot 4\text{H}^+$ moiety may be considered an eight-connected node of the covalently crosslinked network. The topology of HcOF-7 is assigned as a 2-nodal 2D network with a point symbol of $(4^4.8^{16}.12^8)(4)_4$ (Figures 20-21). HcOF-7 exhibits 1D channels along the b -axis with a pore aperture of 5.9×7.2 Å and void space of 20% (Figure 4d), which are large enough for the adsorption of guest molecules such as I_2 ($r \sim 2.0$ Å) and I^- ($r \sim 2.1$ Å).

[0121] In the aqueous environment, I_2 is stabilized by an excess of KI via the triiodide equilibrium ($\text{I}_2 + \text{I}^- \rightleftharpoons \text{I}_3^-$) with an equilibrium constant of 723 M^{-1} . A UV/Vis titration in a solution of $\text{H}_2\text{O}/\text{MeOH} = 99:1$ was performed and the equilibrium constant K_a was measured as 792 M^{-1} at 23°C (Figures 28-29). When HcOF-7 (10 mg) was added to an I_2/KI solution ($0.12 \text{ mM } \text{I}_2 + 0.5 \text{ mM KI}$, 15 mL), the absorption bands attributed to I_2 and I_3^- diminished completely, and the adsorption band of I^- decreased moderately in the UV-Vis spectra (Figures 31-34). The adsorption of iodine/triiodide (I_2/I_3^-) is accelerated (Figure 5a) at higher

temperatures. Compared to the removal of >99 % of iodine/triiodide in 6 h at 23 °C, this process only takes 15 min at 90 °C. The accelerated iodine/triiodide adsorption at higher temperatures is attributed to easier disruption of the hydrogen-bonded network and faster mass transport within the porous material. The adsorption of iodine/triiodide fits with the pseudo-first-order kinetics, and the activation energy barrier of iodine/triiodide adsorption is calculated as 35.3 ± 6.0 kJ/mol (Figure 5a, inset).

[0122] When HcOF-7 was immersed in a concentrated I₂/KI solution (0.87 M I₂ + 1.02 M KI), the weight-increased amount resulting from the total iodine uptake (I₂/I₃⁻/I⁻) was measured as 1.39 ± 0.07 g/g at 23 °C by gravimetric analysis (Figure 5b). At higher temperatures, the weight-increased amounts of HcOF-7 gradually reduced to 1.20 ± 0.06 g/g, and 0.97 ± 0.11 g/g, at 50 and 90 °C, respectively. In comparison, the total iodine adsorptions of active charcoal measured under the same conditions are much lower, at 0.29 ± 0.02 g/g at 23 °C and 0.16 ± 0.02 g/g at 90 °C, respectively (Figure 5b). To reveal the contribution of the crystalline framework of HcOF-7 for total iodine removal, an amorphous analog of HcOF-7 was also synthesized, namely crosslinked hydrogen-bonded organic polymer (CHOP-7, Scheme 3), by crosslinking **1** with EDT followed by HNO₃ protonation. Despite the nearly identical chemical composition to HcOF-7, the total iodine uptakes of CHOP-7 at different temperatures were lower. The weight-increased amounts of CHOP-7 after the uptake of various iodine species were measured as 0.93 ± 0.08 g/g at 23 °C and 0.67 ± 0.03 at 90 °C (Figure 5b). These results highlight the importance of the nitrate dimer containing crystalline framework in promoting total iodine removal.

[0123] In principle, HcOF-7 may remove various iodine species through the direct adsorption of I₃⁻, or the co-adsorption of I₂ and I⁻. To understand the adsorption process, the rates of iodine removal were measured in an H₂O/MeOH = 99:1 solution in the presence of different equivalents of KI (Table 6 and Figures 36-39). In the absence of KI, the rate of I₂ removal was measured as $6.65 \pm 0.30 \times 10^{-4}$ s⁻¹ at 23 °C. When I₂ was mixed with 12 equiv. of KI to increase the population of I₃⁻ to 84% at the initial equilibrium, the iodine removal rate (accounting for I₂ and I₃⁻) decreased to $2.97 \pm 0.06 \times 10^{-4}$ s⁻¹. Furthermore, the iodine removal efficiency of HcOF-7 was reduced from 83% in the absence of KI to 48% in the presence of 12 equiv. of KI (Table 7 and Figure 40). The reduced iodine adsorption rates and efficiencies in the presence of KI indicated that the co-adsorption of I₂ and I⁻ is the major adsorption path, where HcOF-7 adsorbs I₂ in solution via halogen bonding interactions between the I₂ and melaminium moieties, shifting the equilibrium away from the formation of I₃⁻.

[0124] HcOF-7 likely removes I^- through a nitrate-to-iodide (NO_3^-/I^-) exchange. When HcOF-7 (5 mg) was immersed in a KI aqueous solution (3.5 mM, $NO_3^-: I^-$ ratio= 1:1), $27 \pm 1\%$ of NO_3^- in HcOF-7 was exchanged to I^- at $23^\circ C$ (70.7 ± 1.8 mg/g, Figure 5c). After the anion exchange, the N–O stretching band at 1322 cm^{-1} attributed to the NO_3^- decreased significantly in the FT-IR spectra (Figure 43). Despite a moderate NO_3^-/I^- exchange efficiency at equal moles of NO_3^- and I^- , it was noticed that the adsorbed I_2 in HcOF-7 ($I_2 \bullet \text{HcOF-7}$) promotes anion exchange (Figure 5c). $I_2 \bullet \text{HcOF-7}$ samples were prepared by immersing HcOF-7 in the methanolic solutions of I_2 (Figure 45). When samples of $I_2 \bullet \text{HcOF-7}$ (0–0.3 g/g) were employed for the NO_3^-/I^- exchange at $23^\circ C$, the anion exchange efficiency increased from $27 \pm 1\%$ to $37 \pm 2\%$ (Figure 5c). These results indicate that despite iodine adsorption and NO_3^-/I^- exchange taking place separately, the formation of polyiodide (I_3^- and I_5^- , Figure 47) inside HcOF-7 promotes the anion exchange efficiency. After the I_2 adsorption and NO_3^-/I^- exchange, HcOF-7 lost crystallinity due to the disruption of the hydrogen-bonded network (Figure 44).

[0125] To mimic the iodine/iodide removal in water disinfection, an I_2/KI solution was prepared at 5 ppm (I_2 : 3.5 ppm, I^- : 1.5 ppm) and a KI solution at 1.5 ppm before iodine/iodide removal. At this concentration, the population of triiodide is negligible (Table 4). The total residual iodine ($I_2 + I^-$) was measured using the Leuco-crystal violet method (Scheme 4). HcOF-7 showed excellent total iodine removal capabilities for the I_2/KI solutions, and the total residual iodine concentrations were measured as 0.22 ± 0.02 ($23^\circ C$), 0.25 ± 0.02 ($40^\circ C$), 0.32 ± 0.01 ($50^\circ C$), 0.40 ± 0.01 ($70^\circ C$), and 0.45 ± 0.03 ppm ($90^\circ C$) (Figures 5d and 49). In contrast, the total residual iodine concentrations of HcOF-7 for the KI solutions were measured as 0.38 ± 0.02 ($23^\circ C$), 0.48 ± 0.03 ($40^\circ C$), 0.53 ± 0.03 ($50^\circ C$), 0.64 ± 0.01 ($70^\circ C$), and 0.88 ± 0.02 ppm ($90^\circ C$) (Figure 49). These results further support a cooperative iodine/iodide adsorption in HcOF-7. Furthermore, the total residual iodine concentrations of CHOP-7 for the I_2/KI solutions were measured between 1.06 ± 0.02 ($23^\circ C$) and 2.03 ± 0.03 ppm ($90^\circ C$), which are much higher than those of HcOF-7 (Figure 49). This comparison demonstrated the benefit of introducing crystalline framework architectures for collective iodine/iodide removal.

[0126] In natural water, anions such as NO_3^- , $H_2PO_4^-$, SO_4^{2-} , Cl^- , and HCO_3^- may impact the total iodine removal efficiency of HcOF-7. Therefore, to simulate co-existing anions in natural water, NO_3^- (5 ppm), $H_2PO_4^-$ (5 ppm), SO_4^{2-} (20 ppm), Cl^- (80 ppm), HCO_3^- (60 ppm) were added to the I_2/I^- solutions (I_2 : 3.5 ppm, KI: 1.5 ppm) individually and as a

mixture. HcOF-7 crystals (6 mg) were added to these solutions (3 mL). After 72 h, the total residual iodine concentrations (Figure 5d) were measured as 0.30 ± 0.02 , 0.27 ± 0.01 , 0.32 ± 0.02 , 0.38 ± 0.03 , 0.43 ± 0.03 , 0.46 ± 0.02 ppm, respectively. The results confirmed that the total iodine removal efficiency of HcOF-7 remained high in the presence of various

competing anions.

[0127] To quantitatively analyze the dynamic iodine removal capability of HcOF-7 at different temperatures, HcOF-7 columns were prepared for chromatographic breakthrough investigations (Figure 5e). Ball-milled HcOF-7 crystals (240 mg) were packed into a polypropylene plastic column and loaded onto an automatic column chromatography instrument (Figures 54-55). The intake I_2/KI solution (5 ppm) was pre-heated to the desired temperatures in a customized pre-column (Figure 5e) before passing through the HcOF-7 column. Iodinated DI water was injected into the HcOF-7 column continuously with a flow rate of 5 mL/min, and the total residual iodine concentrations were measured at different volume intervals. At 23 °C, the total residual iodine concentrations gradually increased from 0.30 ppm to 0.40 ppm in the first 1.2 L and remained constant for the subsequent 4.8 L until the breakthrough. When the temperature was increased to 50 °C, the total residual iodine concentrations increased from 0.58 ppm to 0.8 ppm for 4.8 L of iodinated water until breakthrough. At 90 °C, the column quickly reached equilibrium in the first 0.72 L intake of iodinated water. The total residual iodine concentration was measured at 0.8 ppm for 4.4 L intake before breakthrough. The faster equilibrated dynamic adsorption at higher temperatures is consistent with the accelerated iodine adsorption rates measured in the temperature-dependent adsorption experiments (Figure 5a). The decreased breakthrough volumes of HcOF-7 columns at higher temperatures are also consistent with their reduced iodine adsorption capacities (Figure 5b). It is worth noting that the breakthrough volumes of HcOF-7 columns are much larger than the activated carbon and activated carbon/anion exchange resin mixed-bed columns (Figure 5f). Furthermore, the high-temperature breakthrough results of HcOF-7 columns are vital for the design of the next-generation iodine filter used in outer space, as the current design in the International Space Station requires pre-chilling of the hot water generated in the reactor before passing through the PWD and reheating water for hot beverages.

[0128] The breakthrough experiment was performed using iodinated tap water (I_2 : 3.5 ppm, I^- : 1.5 ppm) at 23 °C (Figure 5f). The total residual iodine concentrations increased from 0.47 to 0.51 ppm for 3.7 L intake before breakthrough. Compared to iodinated DI water, the total iodine removal efficiency was maintained at ~90% (from 5 ppm of total iodine), and

the breakthrough volume decreased moderately by 23%. After the breakthrough experiment, the adsorbed iodine and iodide species were well-retained in HcOF-7. Possible Iodine leaching was tested by passing 1L tap water through the iodine-containing HcOF-7 column. No significant residual iodine was detected (≤ 0.1 ppm, Figure 56), suggesting that the used amorphous HcOF-7 columns after the iodine and iodide remediation could be recycled for long-term storage of iodine/iodide.

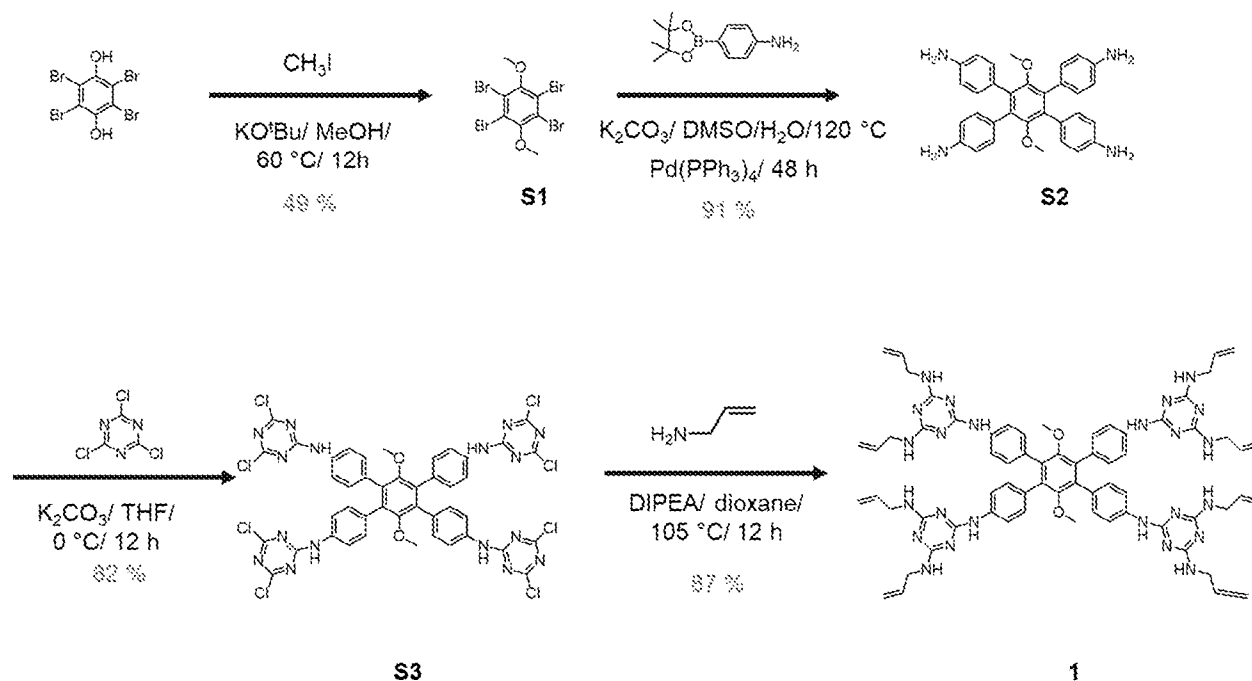
[0129] General information

[0130] All chemical reagents and solvents were purchased from commercial suppliers, including Fisher Scientific, Sigma Aldrich, and VWR, and were used as received.

¹H NMR spectra were recorded on either a Bruker AVIII 500 MHz spectrometer or a Bruker AVIII 600 MHz Spectrometer and referenced to residual solvent peaks. Single crystal diffraction data were collected on an XtaLAB Synergy four-circle diffractometer (Dualflex HyPix detector). Elemental analysis was performed by Intertek Pharmaceutical Services (Whitehouse, NJ). UV/Vis spectroscopy was carried out on a Shimadzu UV-1800 UV/Vis spectrometer. Fourier transform infrared (FT-IR) spectra were recorded on a Jasco 6200 spectrometer. Powder X-ray Diffraction (PXRD) data were collected on the Rigaku MiniFlex powder X-ray diffractometer. Thermogravimetric analysis (TGA) was performed on a TA instrument discovery 55 with samples held in a platinum pan under a nitrogen atmosphere. Data were collected between room temperature and 1000 °C with a ramp rate of 10 °C/min under a nitrogen atmosphere. Supercritical CO₂ activation was performed with a Samdri 795 Critical Point Dryer. Vapor sorption measurements were performed on a Micromeritics FLEX 3.0 surface area analyzer at 297 K.

[0131] Synthesis of monomers

[0132] Scheme 1. Synthesis of compound 1.



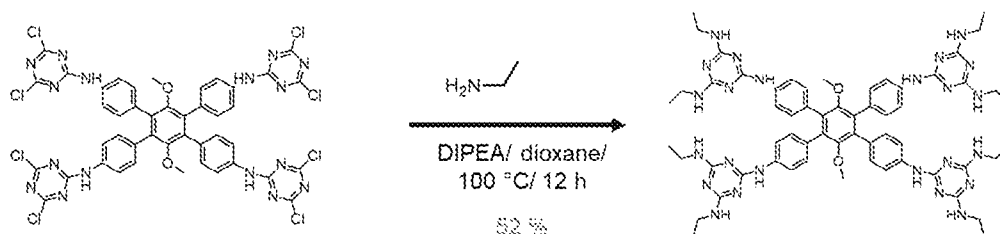
[0133] Synthesis of S1. 2,3,5,6-Tetrabromobenzene-1,4-diol (0.85g, 2.0 mmol) was dissolved in MeOH (15 mL) in a 50 mL round bottom flask. Potassium *tert*-butoxide (0.45 g, 4.0 mmol) and iodomethane (1.2 g, 8.5 mmol) were added to the reaction. The mixture was heated to 50 °C under an N₂ atmosphere. After 12 h, the formed white crystalline solid was collected by filtration and washed with distilled water (50 mL) to yield the product (0.44 g, yield: 49 %). ¹H NMR (DMSO-*d*₆, 500 MHz, 298K) δ (ppm): 3.80 (s, 6H). ¹³C NMR (DMSO-*d*₆, 150 MHz, 298K) δ (ppm): 153.34, 121.89, 61.36.

[0134] Synthesis of S2. Compound S1 (0.91 g, 2.0 mmol), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (1.86 g, 8.5 mmol) and potassium carbonate (1.2 g, 8.7 mmol) were added to a mixture of DMSO (80 mL) and distilled water (20 mL) in a 250 mL round bottom flask at room temperature. The mixture was degassed for 15 min before palladium tetrakis(triphenylphosphine) (35 mg, 0.03 mmol) was added. The reaction was degassed again through three cycles of freeze-pump-thaw before heating to 120 °C under an N₂ atmosphere. After 48 h, the reaction was cooled down to room temperature the solid residues were filtered off. Distilled water (200 mL) was added to the filtrate, and the crude product precipitated. This crude product was collected through filtration, washed with Et₂O (50 mL), and dried under vacuum to yield the product as a grey-colored solid (0.91 g, yield: 91 %). ¹H NMR (DMSO-*d*₆, 500 MHz, 298K) δ (ppm): 6.74 (d, *J* = 6.5 Hz, 8H), 6.36 (d, *J* = 6.5 Hz, 8H), 4.84 (s, 8H), 2.79 (s, 6H). ¹³C NMR (DMSO-*d*₆, 150 MHz, 298K) δ (ppm): 152.46, 147.19, 135.78, 132.10, 125.59, 113.93, 59.77. HR-ESI-MS: calculated for [M + H]⁺ *m/z* = 503.2402, found *m/z* = 503.2448.

[0135] Synthesis of S3. Cyanuric chloride (0.83 g, 4.5 mmol) and potassium carbonate (2.4 g, 17 mmol) were added to anhydrous THF (40 mL) in a 250 mL round bottom flask at 0 °C. Compound **S2** (1.0 g, 2.0 mmol) dissolved in THF (60 mL) was added to the reaction using a dropping funnel slowly over 15 min. The reaction was stirred for 12 h, and the temperature was allowed to warm to room temperature. After then, the solid residue was filtered off. The filtrate was collected, and the organic solvent was removed under reduced pressure. The solid residue was washed thoroughly with distilled water (250 mL) to afford the product as yellow solid (1.8 g, yield: 82%). ¹H NMR (DMSO-*d*₆, 500 MHz, 298 K) δ (ppm): 11.11 (s, 4H), 7.52 (d, *J* = 7.0 Hz, 8H), 7.22 (d, *J* = 7.0 Hz, 8H), 2.87 (s, 6H). ¹³C NMR (DMSO-*d*₆, 150 MHz, 298K) δ (ppm): 154.35, 151.82, 135.94, 135.45, 132.62, 131.53, 120.10, 60.24. HR-ESI-MS: calculated for [M + H]⁺ *m/z* = 1094.9947, found *m/z* = 1094.9928.

[0136] Synthesis of 1. Compound **S3** (1.1 g, 1.0 mmol), allylamine (0.91 g, 16.0 mmol), and *N,N*-diisopropylethylamine (1.0 g, 8 mmol) were dissolved in dioxane (100 mL) in a 250 mL round bottom flask. The reaction was heated to 105 °C under an N₂ atmosphere. The reaction was cooled down to room temperature after 12 h, and distilled water (200 mL) was added to the reaction mixture to generate a light-yellow precipitate. The product was collected through filtration, washed with Et₂O (30 mL), and dried in the open air (1.1 g, yield: 87%). ¹H NMR (DMSO-*d*₆, 500 MHz, 298 K) δ (ppm): 8.83 (m, 4H), 7.65 (s, 8H), 6.98 (d, *J* = 8.0 Hz, 8H), 6.89 (m, 8H), 5.87 (m, 8H), 5.12 (d, *J* = 17.0 Hz, 8H), 5.02 (d, *J* = 10.5 Hz, 8H), 3.87 (t, *J* = 5.5 Hz, 16H), 2.83 (s, 6H). ¹³C NMR (DMSO-*d*₆, 150 MHz, 298K) δ (ppm): 165.96, 164.44, 151.99, 139.37, 136.77, 135.44, 131.01, 129.78, 118.40, 115.05, 59.80, 42.92. HR-ESI-MS: calculated for [M + H]⁺ *m/z* = 1259.6500, found *m/z* = 1259.6460.

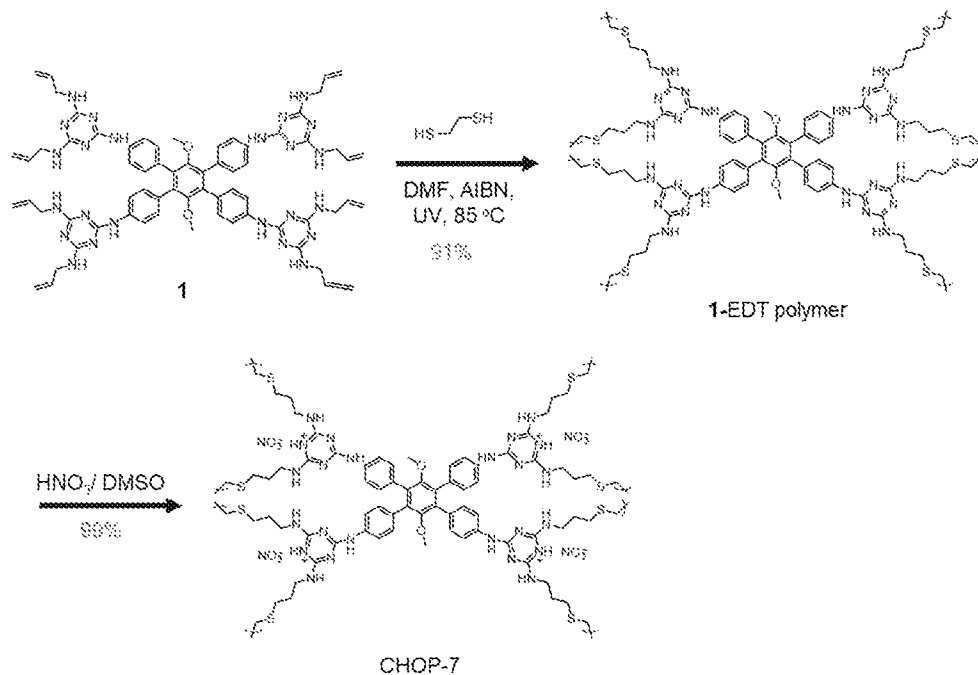
[0137] Scheme 2. Synthesis of compound 2.



[0138] Synthesis of 2. Compound **S3** (150 mg, 0.12 mmol) and ethyl amine THF solution (2M, 1 mg, 2 mmol), and *N,N*-diisopropylethylamine (250 mg, 2 mmol) were dissolved into 1,4-dioxane (30 mL) in a Schlenk tube. The Schlenk tube was sealed and heated to 100 °C for 12h. Then the solvents are removed under reduced pressure. The crude product was washed with Et₂O (30 mL) and distilled water (50 mL) to yield a light-yellow

product (72.5 mg, yield: 52%). ^1H NMR ($\text{DMSO}-d_6$, 500 MHz, 298 K) δ (ppm): 8.78 (m, 4H), 7.65 (d, $J = 8.0$ Hz, 8H), 6.98 (d, $J = 8.0$ Hz, 8H), 6.78 (m, 8H), 3.25 (s, 16H), 2.82 (s, 6H), 1.07 (m, 24H).

[0139] Scheme 3. Synthesis of CHOP-7.



5

[0140] Synthesis of CHOP-7. Compound **1** (200.0 mg, 0.16 mmol) was dissolved in the NMP (3 mL, anhydrous) in a Schlenk tube. EDT (63.1 mg, 0.67 mmol, 4.2 *equiv.*) and azobisisobutyronitrile (AIBN, 5.0 mg, 0.03 mmol) were added to the solution. The mixture was degassed and filled with N_2 , irradiated under the UV light for 48 h, and heated at 85°C for 12h. After that, the formed precipitate was collected by filtration and washed with DMSO (10 mL $\times$ 3) and THF (10 mL $\times$ 3). After freeze drying, the 1-EDT polymer was obtained (236.4 mg, 91%). The polymer was active by supercritical CO_2 three times and characterized by IR, TGA, and elemental analysis. Elemental analysis: $1 \cdot [\text{EDT}]_{3.7} [\text{CO}_2]_{1.9}$, calculated: C 54.89%, H 5.73%, N 19.87%, S 14.02%; found: C 56.72%, H 5.66%, N 18.02%, S 12.17%.

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[0141] The obtained polymer and fuming HNO_3 (90%, 1.5 g, 21.4 mmol) were mixed in DMSO (10 mL). After 12 h, the solid was collected by filtration and washed with THF (10 mL $\times$ 3) to yield the CHOP-7 as a yellow solid (311.0 mg, 99%).

15

[0142] Preparation of precursor crystals

[0143] X-ray diffraction data of crystals were collected from XtaLAB Synergy

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Dualflex single-crystal X-ray diffractometer at 100 K with Cu $K\alpha$ radiation ($\lambda = 1.54184\text{\AA}$). Multi-scan absorption corrections were applied in each case. The structures were solved by SHELXT and refined with SHELXL using the program Olex2. All non-hydrogen atoms of

the monomers were refined anisotropically. The hydrogen atoms were modeled at geometrically constrained positions and refined using the riding model. Details of each crystal structure will be discussed in the section below. CCDC contains supplementary crystallographic data, which can be accessed through the Cambridge Crystallographic Data Centre at <https://www.ccdc.cam.ac.uk/>. The topology of $1 \cdot 4H^+ \cdot 4NO_3^-$ crystal is solved by *Topospro* software. The nitrate dimer was simplified as one node to connect different $1 \cdot 4H^+$ monomers. The $1 \cdot 4H^+ \cdot 4NO_3^-$ crystal is crystallized in *flu* (fluorite) topology. Each $1 \cdot 4H^+$ is connected with eight nitrate dimers, while each nitrate dimer is connected with four $1 \cdot 4H^+$.

[0144] Crystallization of 1_{crystal} . Compound **1** (50.0 mg, 0.04 mmol) was dissolved in the DMSO (5 mL) in a 20 mL vial. The vial was placed in a 100 mL vial with MeOH for solvent diffusion at room temperature. Transparent block crystals of 1_{crystal} were obtained after 5 d.

[0145] Table 1. Single-crystal X-ray diffraction data of 1_{crystal} , $1 \cdot 4H^+ \cdot 4NO_3^-$ crystal, and HcOF-7.

Identification code	1_{crystal}	$1 \cdot 4H^+ \cdot 4NO_3^-$ crystal	HcOF-7
CCDC number	2176150	2176149	2175909
Empirical formula	$C_{68}H_{74}N_{24}O_2$	$C_{92}H_{124}N_{28}O_{26}$	$C_{95}H_{137}N_{28}O_{14}S_8$
Formula weight	1259.51	2038.18	2151.80
Temperature/K	100.00(10)	100.00(10)	100.00(10)
Crystal system	monoclinic	triclinic	triclinic
Space group	P2 ₁ /n	P-1	P-1
<i>a</i> /Å	15.0148(13)	10.3450(3)	10.8379(2)
<i>b</i> /Å	14.7706(8)	15.3223(5)	15.5881(3)
<i>c</i> /Å	16.4854(11)	16.9447(8)	17.4865(3)
α /°	90	77.089(4)	76.293(2)
β /°	103.120(8)	77.183(3)	72.832(2)
γ /°	90	81.122(3)	79.225(2)
Volume/Å ³	3560.7(4)	2537.20(17)	2720.32(10)
<i>Z</i>	2	1	1
$\rho_{\text{calc}}/\text{cm}^3$	1.175	1.335	1.314
μ/mm^{-1}	0.613	0.832	2.113
<i>F</i> (000)	1332.0	1082	1143.0
Crystal size/mm ³	0.1 × 0.1 × 0.05	0.3 × 0.2 × 0.2	0.1 × 0.08 × 0.05
Radiation	CuK α (λ = 1.54184)	CuK α (λ = 1.54184)	CuK α (λ = 1.54184)
2 θ range for data collection/°	7.194 to 119.994	5.454 to 154.756	5.392 to 154.364

Index ranges	$-16 \leq h \leq 16, -16 \leq k \leq 12, -18 \leq l \leq 18$	$-13 \leq h \leq 10, -18 \leq k \leq 19, -20 \leq l \leq 21$	$-12 \leq h \leq 13, -19 \leq k \leq 18, -22 \leq l \leq 21$
Reflections collected	17854	26975	35749
Independent reflections	5270 [$R_{\text{int}} = 0.1305, R_{\text{sigma}} = 0.1462$]	10154 [$R_{\text{int}} = 0.0556, R_{\text{sigma}} = 0.0603$]	10783 [$R_{\text{int}} = 0.0311, R_{\text{sigma}} = 0.0305$]
Data/restraints/parameters	5270/0/425	10154/472/769	10783/733/722
Goodness-of-fit on F^2	0.924	1.198	1.699
Final R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0960, wR_2 = 0.2196$	$R_1 = 0.1016, wR_2 = 0.2857$	$R_1 = 0.1527, wR_2 = 0.4073$
Final R indexes [all data]	$R_1 = 0.2426, wR_2 = 0.3023$	$R_1 = 0.1240, wR_2 = 0.3143$	$R_1 = 0.1745, wR_2 = 0.4298$
Largest diff. peak/hole / e $\text{\AA}^{-3}$	0.20/-0.20	0.55/-0.51	0.70/-0.64

[0146] Crystallization of $1 \cdot 4\text{H}^+ \cdot 4\text{NO}_3^-$ crystal. Monomer **1** (50.0 mg, 0.13 mmol) was dissolved in the mixture of 1,4-dioxane (5 mL) and fuming nitric acid (0.1 mL). The solution was filtered to remove any insoluble residues and then added to a 20 mL vial. This vial was placed in a 100 mL vial with Et_2O for solvent diffusion at room temperature. Yellow block crystals of $1 \cdot 4\text{H}^+ \cdot 4\text{NO}_3^-$ crystal were obtained after 3 d.

[0147] PXRD investigation of the stability of $1 \cdot 4\text{H}^+ \cdot 4\text{NO}_3^-$ crystal. The single crystals of $1 \cdot 4\text{H}^+ \cdot 4\text{NO}_3^-$ (5 mg) were added to 3 mL 1,4-dioxane, cyclohexane, THF, Et_2O , and EtOAc for 24 hours. PXRD profiles of each sample were collected. The crystallinity of $1 \cdot 4\text{H}^+ \cdot 4\text{NO}_3^-$ crystal decreased significantly in Et_2O and EtOAc . In addition, the crystallinity of $1 \cdot 4\text{H}^+ \cdot 4\text{NO}_3^-$ crystal significantly reduced in the open air.

[0148] Table 2. Distances of the nearby alkene carbon atoms in the lattice of $1 \cdot 4\text{H}^+ \cdot 4\text{NO}_3^-$ crystal.

alkene carbon atom		symmetry operation	distance ($\text{\AA}$)	alkene carbon atom		symmetry operation	distance ($\text{\AA}$)
C4	C1	x, y, z	7.908	C1	C34	2-x, 1-y, 1-z	9.3479
C4	C34	-1+x, y, z	8.0512	C1	C4	1+x, y, z	9.8179
C4	C1	-x, 1-y, 1-z	8.2764	C1	C4	-1-x, 2-y, 1-z	9.8337
C4	C1	-x, 2-y, 1-z	8.6343	C1	C4	x, y, 1+z	9.8929
C4	C31	-x, 1-y, -z	8.6689	C31	C1	-x, 1-y, 1-z	4.4919
C4	C4	-1-x, 2-y, 1-z	8.8349	C31	C34	-1+x, y, z	6.7889
C4	C34	-x, 1-y, 1-z	9.3736	C31	C1	1-x, 1-y, 1-z	7.2433

C4	C31	-1+x, 1+y, z	9.4597	C31	C1	1+x, y, -1+z	7.4341
C4	C34	-2+x, 1+y, z	9.4672	C31	C1	x, y, -1+z	7.9848
C4	C31	-x, 1-y, 1-z	9.7334	C31	C4	-x, 1-y, -z	8.6689
C4	C34	1-2+x, y, z	9.8049	C31	C34	2-x, 1-y, -z	9.2472
C4	C1	-1+x, y, z	9.8179	C31	C4	1+x, -1+y, z	9.4597
C4	C1	-1-x, 2-y, 1-z	9.8337	C31	C4	-x, 1-y, 1-z	9.7334
C4	C1	x, y, -1+z	9.8929	C31	C31	-x, 1-y, -z	9.8758
C1	C34	1-x, 1-y, 1-z	4.4617	C34	C1	1-x, 1-y, 1-z	4.4617
C1	C31	-x, 1-y, 1-z	4.4919	C34	C34	2-x, 1-y, 1-z	5.9856
C1	C31	1-x, 1-y, 1-z	7.2433	C34	C31	1+x, y, z	6.7889
C1	C31	-1+x, y, 1+z	7.4341	C34	C4	1+x, y, z	8.0512
C1	C4	x, y, z	7.908	C34	C1	1+x, y, z	8.2268
C1	C31	x, y, 1+z	7.9848	C34	C31	2-x, 1-y, -z	9.2472
C1	C34	-1+x, y, z	8.2268	C34	C1	2-x, 1-y, 1-z	9.3479
C1	C4	-x, 1-y, 1-z	8.2764	C34	C4	-x, 1-y, 1-z	9.3736
C1	C1	-x, 1-y, 2-z	8.3866	C34	C4	2+x, -1+y, z	9.4672
C1	C4	-x, 2-y, 1-z	8.6343	C34	C4	2+x, y, z	9.8049

[0149] **SCSC synthesis of H_COF-7.**

[0150] **Solvent exchange of 1·4H⁺·4NO₃⁻crystal.** In order to remove the dioxanes, single crystals of 1·4H⁺·4NO₃⁻ (10 mg) were immersed in THF and cyclohexane (10 mL×3) separately. After 12 h, the crystals were filtered off and dried in the open air for 2 h. The obtained crystals were dissolved in DMSO-*d*₆ for ¹H NMR analysis. The result shows dioxane could be effectively replaced by THF, while cyclohexane cannot replace it. After THF exchange, 1·4H⁺·4NO₃⁻crystal was immersed in cyclohexane (10 mL×3) for 12 h. ¹H NMR shows THF remained.

[0151] **Crosslinker diffusion.** Single crystals of 1·4H⁺·4NO₃⁻crystal were washed with THF (10 mL × 3) for 12h to allow an extensive solvent exchange. A cyclohexane solution (3 mL) of 1,2-ethanedithiol (EDT, 300 μL) was added to the samples in a vial (~40 mg). After 72h, the crystals were filtered off and dried in the open air for 6 h. The crystals were dissolved in DMSO-*d*₆ and characterized by ¹H NMR.

[0152] Optimization of the synthesis of single-crystalline HcOF-7. In order to remove the dioxanes in $1 \cdot 4\text{H}^+ \cdot 4\text{NO}_3^-$ crystal, single crystals were washed with THF three times ($10 \text{ mL} \times 3$) to allow an extensive solvent exchange. A cyclohexane solution (3 mL) of 1,2-ethanedithiol (EDT) was added to the samples in a vial ($\sim 40 \text{ mg}$). The synthesis of HcOF-7 was performed at various concentrations of EDT in cyclohexane solutions (33.3, 50, 58.3, 100, and $133.3 \text{ }\mu\text{L/mL}$) for the extensive crosslinking. The EDT-diffused crystal samples were kept in the dark for 72 h to allow for extensive EDT diffusion. Next, the vials were irradiated under UV light (medium-pressure 175-watt Hg lamp) for 48 h with forced air cooling. The crystal samples were collected and washed with an excess of THF and hexanes to remove the unreacted EDT. The HcOF-7 crystals were further characterized by PXRD, IR spectrum, Raman spectrum, TGA, and solid-state ^{13}C NMR, δ (ppm): 162.10, 155.40, 181.86, 132.59, 121.19, 119.12, 110.69, 60.19, 40.57, 30.07.

[0153] Table 3. Summary of the elemental analyses of HcOF-7 synthesized at various EDT concentrations.

concentration of EDT	Composition	Cal. (%)	Found (%)	Degree of crosslinking ^a
33.3 $\mu\text{L/mL}$	$1 \cdot 4\text{H}^+ \cdot [\text{NO}_3^-]_4 \cdot [\text{EDT}]_{3.05} \cdot [\text{CO}_2]_{3.1}$	C 47.59, H 5.35, N 19.97, S 9.82	C 47.01, H 5.02, N 20.27, S 10.11	76 %
50.0 $\mu\text{L/mL}$	$1 \cdot 4\text{H}^+ \cdot [\text{NO}_3^-]_4 \cdot [\text{EDT}]_{3.1} \cdot [\text{CO}_2]_{2.2}$	C 48.02, H 5.44, N 20.42, S 10.15	C 48.29, H 5.12, N 20.64, S 10.46	78 %
58.3 $\mu\text{L/mL}$	$1 \cdot 4\text{H}^+ \cdot [\text{NO}_3^-]_4 \cdot [\text{EDT}]_{3.3} \cdot [\text{CO}_2]_{2.95}$	C 47.43, H 5.34, N 20.06, S 10.61	C 47.71, H 5.05, N 20.09, S 10.84	83 %
100.0 $\mu\text{L/mL}$	$1 \cdot 4\text{H}^+ \cdot [\text{NO}_3^-]_4 \cdot [\text{EDT}]_{3.8} \cdot [\text{CO}_2]_{2.3}$	C 47.26, H 5.43, N 19.65, S 12.09	C 47.78, H 5.16, N 19.9, S 12.36	95 %
133.2 $\mu\text{L/mL}$	$1 \cdot 4\text{H}^+ \cdot [\text{NO}_3^-]_4 \cdot [\text{EDT}]_{3.95} \cdot [\text{CO}_2]_{2.25}$	C 47.13, H 5.43, N 19.6, S 12.52	C 47.34, H 5.17, N 19.78, S 12.77	99 %

[a] Degree of cross-linking = $n[\text{EDT}] / 4 \times 100\%$

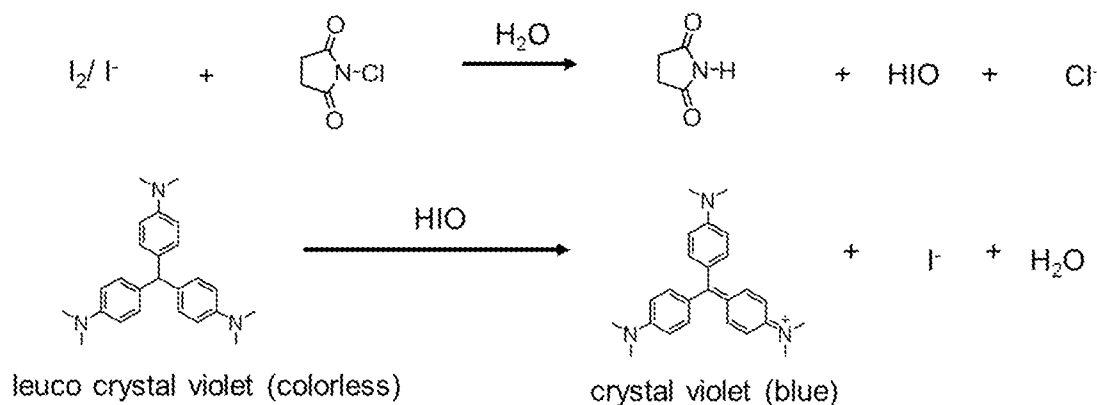
[0154] Porosity analysis.

[0155] HcOF-7 crystals ($\sim 45 \text{ mg}$) were immersed in a 20 mL vial with THF (15 mL). Then THF was piped out and refilled every 8 hours three times. After solvents exchanging,

the HcOF-7 crystals were activated under vacuum at 90 °C for 24 h. Gas/vapor sorption measurements were performed on a Micromeritics FLEX 3.0 surface area analyzer. The CO₂ sorption and other vapor sorption isotherms were measured at room temperature.

[0156] Iodine and iodide sorption investigations. The residue of iodine and iodide is determined by the Leuco-crystal violet method. The solution preparation and measurement procedures are described below.

[0157] Scheme 4. Mechanism of Leuco-crystal violet method for I₂/ I⁻ residue determination.



[0158] Preparation of the standard iodide solution. A 15 ppm I⁻ the stock solution was prepared by dissolving 19.6 mg of potassium iodide (dried at 105 °C for 1 h) in 1 L of deionized water. Then the solution was diluted to 0.1 to 0.5 ppm for the standard curve calibration.

[0159] Preparation of the buffer solution. A pH 4.0 buffer solution was prepared in a 50 mL volumetric flask by dissolving 1.70 grams of potassium dihydrogen phosphate (KH₂PO₄) in distilled water (30 mL). Phosphoric acid (85 %, 1 mL) was added to the solution. Then the solution was diluted to exactly 50 mL.

[0160] Preparation of the Leuco-crystal violet solution. Phosphoric acid (85%, 0.25 mL), Leuco-crystal violet, 4,4',4''-methylidynetris (25 mg, 0.067 mmol) were added to a 100 mL volumetric flask with distilled water (30 mL) and shaken until the solid completely dissolved. The solution was then diluted to exact 100 mL.

[0161] Preparation of the N-Chlorosuccinimide-Succinimide solution. N-chlorosuccinimide (100 mg, 0.75 mmol) and succinimide (1.0 g, 10.1 mmol) were dissolved in 75 mL distilled water in a 100 mL volumetric flask. Then the solution was diluted to 100 mL with distilled water.

[0162] Residual concentration of [I₂ + I⁻] measurement. Distilled water (2 mL) and iodinated water (1 mL) were mixed in a 4 mL vial. Then the phosphate buffer solution (0.1

mL) and N-chlorosuccinimide-succinimide reagent solution (0.1 mL) were added to the vial. The solution was shaken after adding the Leuco-crystal violet solution (0.1 mL). The UV/Vis absorbance was measured at 592 nm at 25 °C exactly 10 min after Leuco-crystal violet was added. The residue of $[I_2 + I^-]$ could be calculated based on the calibration curve.

5 **[0163]** Dual-wavelength UV/Vis spectrometry is a simpler method to measure I^- concentration in the presence of NO_3^- interference. When I^- or NO_3^- is directly determined by UV/Vis spectrometry, the two anions interfere due to the absorption band overlap. Therefore, a dual-wavelength method with primary wavelength (220 nm) and secondary wavelength (231 nm) was used to determine NO_3^- and I^- in solution. Based on the UV/Vis spectra of
10 standard KI (0.07 mmol/L) solution, standard KNO_3 (0.07 mmol/L) solution and KI (0.07 mmol/L) + KNO_3 (0.07 mmol/L) mixture (Figure 27), the linear equations were calculated as $A_{220nm} - A_{231nm} = 2.960 c(NO_3^-)$, $A_{220nm}(NO_3^-) = 3.667 c(NO_3^-)$, and $A_{220nm}(I^-) = A_{220nm} - A_{220nm}(NO_3^-) = 10.666 c(I^-)$. The result is in good agreement with the previously reported data.

15 **[0164]** **Study of KI_3 formation equilibrium constant in an $H_2O/MeOH$ (99:1) solution**

[0165] To increase the solubility of iodine in the aqueous environment, an $H_2O/MeOH$ (99:1) solution of I_2 was prepared. The equilibrium constant of KI_3 formation was measured by UV/Vis titration. I_2 (150 mg, 0.59 mmol) was dissolved in MeOH (10 mL), and
20 990 mL of H_2O was added to the solution. Different amounts of KI (0 to 12 equiv.) were added to the solution, and the UV/Vis spectra were recorded using a 0.1 cm cuvette (Figure 28-29). The peaks attributed to I_3^- at 292 and 354 nm were fitted with the 1:1 binding model. The equilibrium constant K in $H_2O/MeOH$ (99:1) solution is calculated as $792 \pm 20 M^{-1}$.

[0166] Different I_2/I^- solutions were prepared for the investigation of iodine/iodide
25 uptake capacities, temperature-dependent adsorption rate determinations, and low-concentration total iodine removal. The concentrations of the I_2 , I^- , and I_3^- at equilibrium were calculated based on the equilibrium constant and listed in Table 4.

[0167] **Table 4.** Summary of the concentrations of I_2 , I^- and I_3^- species at equilibrium.

experiments	input amounts of I_2 and I^-	concentrations of $[I_2]/[I^-]/[I_3^-]$
uptake capacity studies	I_2 : 0.87 M	I_2 : 0.0076 M
	KI: 1.02 M	I^- : 0.1576 M I_3^- : 0.8624 M
kinetic studies	I_2 : 0.12 mM	I_2 : 0.09 mM
	KI: 0.50 mM	I^- : 0.47 mM

		I ₃ ⁻ : 0.03 mM
Iodine residue removal	I ₂ : 3.5 mg/L 13.8 μM	I ₂ : 13.7 μM
	KI: 1.5 mg/L 11.8 μM	I ⁻ : 11.7 μM
		I ₃ ⁻ : 0.12 μM

[0168] Kinetic study of iodine adsorption. I₂/KI solution (0.12 mM I₂ + 0.50 mM KI, 15 mL) was prepared and added to a 20 mL sealed vial with string. The concentration of I₂, I⁻, and KI₃ is calculated as 0.089, 0.470, and 0.030 mM, respectively. The sealed vials were heated to 23, 40, 50, 70, and 90 °C in the oil bath. When the temperature stabilized, 10 mg HcOF-7 was added to the vials, and the timer was started. Periodically, 3 mL of the solution was piped out for concentration measurement by UV/Vis spectroscopy at 292 nm. The solution was added back into the vial after the measurement. A pseudo-first-order equation was used to fit the adsorption results at different temperatures (Figure 31-34).

$$r = -\frac{d[c]}{dt} = k[c]$$

$$\ln \frac{c_0}{[c]} = kt$$

k : rate constant; $[c]$: concentration; c_0 : initial concentration.

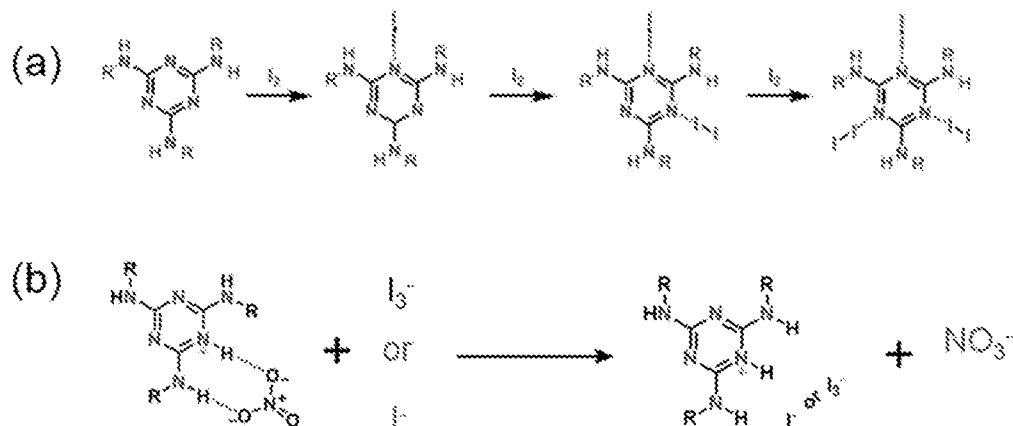
The obtained rate constant was further fitted by the Arrhenius equation (Figure 35):

$$\ln k = \frac{-E_a}{RT} + \ln A$$

E_a : activation energy; k : rate constant; A : pre-exponential factor. The activation energy is calculated as 35.3 ± 6.0 kJ/ mol.

[0169] Iodine uptake amount measurements. To study the total iodine uptake of different absorbents at different temperatures in an aqueous environment, HcOF-7 crystals (10 mg), activated carbon (15 mg), and CHOP-7 (10 mg) powder were soaked in a 3 mL I₂/KI concentrated aqueous solution (0.51 g KI and 0.66 g I₂) in a 4 mL vial at 23, 40, 50, 70 and 90 °C for 48 h. The solid was collected by filtration, washed with excess water until the filtrate became colorless, and dried in the open air before weighing. The [I₂ + I⁻] uptake amount was measured by the gravimetric method. The experiment was repeated three times. After adsorption at 23, 40, 50, 70 and 90 °C, the HcOF-7@[I₂ + I⁻] were weighted as 23.9 ± 0.7 , 23.0 ± 0.3 , 22.1 ± 0.6 , 22.0 ± 0.2 , and 19.7 ± 0.7 mg, , respectively. The CHOP-7@[I₂ + I⁻] obtained at 23, 40, 50, 70 and 90 °C were weighted as 19.3 ± 0.8 , 18.6 ± 0.6 , 18.0 ± 0.3 , 17.3 ± 0.3 , and 16.7 ± 0.3 mg, respectively. The activated carbon@I₂ obtained at 23, 40, 50, 70 and 90 °C were weighed as 19.4 ± 0.3 , 18.8 ± 0.3 , 18.4 ± 0.5 , 17.9 ± 0.3 , and 17.4 ± 0.3 mg, respectively.

[0170] **Scheme 5.** (a) The halogen bond interaction between I₂ and the triazine rings of HcOF-7. (b) I₃⁻ or I⁻ exchange process with HcOF-7.



[0171] **Table 5.** List of porous materials and their iodine species uptake capacities from aqueous solution.

Type of materials	Compound name	Guest molecules	Capacity
HcOF	HcOF-1	I ₂	2.9 g/g
HcOF	HcOF-2	I ₂	3.2 g/g
HcOF	HcOF-3	I ₂	3.0 g/g
HcOF	HcOF-4	I ₂	3.6 g/g
POP	CaCOP1	I ₂	2.4 g/g
POP	CaCOP2	I ₂	2.81 g/g
POP	CaCOP3	I ₂	3.1 g/g
POP	C[4]P-BT	I ₂	2.32 g/g
POP	C[4]P-BTP	I ₂	3.24 g/g
POP	C[4]P-TTP	I ₂	2.51 g/g
POP	C[4]P-BP	I ₂	2.37g/g
POP	C[4]P-TPE	I ₂	2.99 g/g
POP	C[4]P-DPP	I ₂	1.58 g/g
POP	CalCOP1	I ₂	2.32 g/g
POP	CalCOP2	I ₂	1.76 g/g
POP	CalCOP3	I ₂	0.35 g/g
POP	CalCOP4	I ₂	0.16 g/g
POP	TNHCP1	I ₂	0.73 g/g
POP	TNHCP2	I ₂	0.85 g/g
POP	TNHCP3	I ₂	0.72 g/g
MOF	[Mn ₂ (oxdz) ₂ (tphn)(H ₂ O)]·CH ₃ OH _n	I ₂	1.1 g/g
MOF	MBM - MOF	I ₂	0.88 g/g
POP	Compound-1	I ₃ ⁻	3.5g/g
POP	Compound-2	I ₃ ⁻	3.04 g/g
POP	NTP	I ₃ ⁻	0.43g/g
MOF	cadmium(II)-triazole MOF	I ₃ ⁻	0.18 g/g
HcOF	HcOF-7	I ₂ + I ⁻	1.39 g/g
resin	SiPyR-N4	I ⁻	0.15 g/g

resin	H.M.W. resin	I ⁻	0.64 g/g
resin	D201	I ⁻	0.31 g/g
resin	Ag-D201	I ⁻	0.26 g/g
MOF	Ag ₂ O-Ag ₂ O ₃ @ZIF-8	I ⁻	0.23 g/g
MOF	MIL-101(Cr)-SO ₃ Ag	I ⁻	0.24 g/g
MOF	AgII@MIL101	I ⁻	0.04 g/g
Nano particle	Ag ₂ O@Mg(OH) ₂	I ⁻	0.37 g/g
Nano particle	Ag ₂ O@titanate nanolamina	I ⁻	0.43 g/g
Nano particle	AgCl@calcium alginate	I ⁻	0.11 g/g
aerogel	Ag@silica aerogel	I ⁻	0.09 g/g
Activated carbon	Ag@activated carbon	I ⁻	0.04 g/g

[0172] Kinetic study of I₂ adsorptions in the presence of the different amounts of

KI. There are two possible paths for collective iodine and iodide adsorption in HcOF-7: (1) simultaneous adsorption of I₂ through halogen bonding interaction and nitrate-to-iodide anion exchange, and (2) nitrate-to-triiodide anion exchange in addition to I₂ adsorption. To reveal the adsorption path, I₂ aqueous solutions (1% MeOH) with different amounts of KI (0 to 12 equiv.) were prepared. The initial concentrations of [I₂], [I⁻], and [I₃⁻] are summarized in Table 6.

[0173] Specifically, I₂ (150 mg, 0.59 mmol) was dissolved in MeOH (10 mL), and 990 mL H₂O was added to dilute the solution. Stock solutions of 0.59 mM I₂ with 0, 0.59, 1.18, and 7.08 mM (0 to 12 equiv.) of KI were prepared by adding 0, 98.0, 196.0 and 1176.5 mg KI to the I₂ solution. HcOF-7 (10 mg) was added to each solution (15 mL) in a vial with stirring. 3 mL solution was periodically withdrawn for UV/Vis measurement (Figure 36-39). The solution was added back to the vial after each measurement. The 460 and 400 nm absorbance were used to fit the pseudo-first-order kinetics (Figure 36-39), and the results were summarized in Table 6.

[0174] Table 6. The rate constants of total iodine (I₂ and I₃⁻) removal using HcOF-7.

input amounts of I ₂ and I ⁻	concentrations of [I ₂]/[I ⁻]/[I ₃ ⁻]	rate constant (×10 ⁻⁴ s ⁻¹)
I ₂ : 0.59 mM	I ₂ : 0.59 mM	6.65 ± 0.30 ^a
I ₂ : 0.59 mM KI: 0.59 mM	I ₂ : 0.438 mM I ⁻ : 0.438 mM I ₃ ⁻ : 0.152 mM	6.11 ± 0.23 ^a 6.20 ± 0.12 ^b
I ₂ : 0.59 mM KI: 1.18 mM	I ₂ : 0.340 mM I ⁻ : 0.940 mM I ₃ ⁻ : 0.250 mM	5.93 ± 0.21 ^a 6.30 ± 0.05 ^b
I ₂ : 0.59 mM KI: 7.08 mM	I ₂ : 0.095 mM I ⁻ : 6.685 mM I ₃ ⁻ : 0.495 mM	2.97 ± 0.06 ^a 2.93 ± 0.06 ^b

^aThe rate constant is calculated using the absorbance at 460 nm. ^bThe rate constant is calculated using the absorbance at 400 nm.

[0175] The static removal efficiency of I₂ in the presence of different amounts of KI. The static removal efficiency of I₂ in the presence of different amounts of KI (0 to 12 equiv.) was also investigated. In this investigation, the I₂ is more than the HcOF-7 adsorption capacity.

[0176] Specifically, I₂ (200 mg, 0.79 mmol) was dissolved in MeOH (10 mL), and 990 mL of H₂O was added to dilute the mixture. Stock solutions of 0.79 mM I₂ with 0, 1.57, 3.94, and 9.45 mM of KI were prepared by adding 0, 260.6, 654.0, and 1568.7 mg KI to the I₂ solution. To 50 mL of each solution in the vials, HcOF-7 (5 mg) was added. After shaking for 72 h, the removal efficiency was calculated by measuring the UV/Vis absorbance before and after adding HcOF-7 (Figure 40). The results are summarized in Table 7. The I₂ removal efficiency continuously decreased from 83% to 48% in the presence of KI, suggesting HcOF-7 adsorb I₂ and I⁻ collectively rather than removing I₃⁻ from the aqueous solution.

[0177] Table 7. Iodine (I₂ and I₃⁻) removal efficiency of HcOF-7

$[I_2]_0/[I^-]_0$ concentrations	equilibrated concentrations of $[I_2]/[I^-]/[I_3^-]$	I ₂ /I ₃ ⁻ Removal efficiency
I ₂ : 0.79 mM	I ₂ : 0.79 mM	83.0% ^a
I ₂ : 0.79 mM KI: 1.57 mM	I ₂ : 0.405 mM I ⁻ : 1.192 mM I ₃ ⁻ : 0.382 mM)	68.8% ^b
I ₂ : 0.79 mM KI: 3.94 mM	I ₂ : 0.215 mM I ⁻ : 3.364 mM I ₃ ⁻ : 0.573 mM	62.6% ^b
I ₂ : 0.79 mM KI: 9.45 mM	I ₂ : 0.099 mM I ⁻ : 8.761 mM I ₃ ⁻ : 0.688 mM	48.2% ^b

^aThe removal efficiency is calculated based on the absorbance at 460 nm. ^bThe removal efficiency is calculated based on the absorbance at 354 nm.

[0178] Investigation of NO₃⁻ to I⁻ anion exchange in HcOF-7. Activated HcOF-7 (5 mg) crystals were added to 3 mL of 3.5 mM KI solution in a 4 mL vial. The amount of I⁻ in solution and NO₃⁻ in HcOF-7 is kept at a 1:1 molar ratio. The samples were kept at room temperature (23 °C) or heated to desired temperatures (50 and 90 °C) in an oil bath. After 72 h, the residue iodine concentrations of the solutions and the amounts of I⁻ uptake were measured using the dual-wavelength UV/Vis spectroscopy method. The experiments were repeated four times.

[0179] Regeneration of HcOF-7. To remove the guests, I₂/I⁻•HcOF-7 was deprotonated by NaOH (0.5 M) in DMSO/MeOH solution (V_(DMSO): V_(MeOH)= 1:1) until the

color of the crystals changed to light yellow. Then, HcOF-7 was re-protonated by a DMSO solution of HNO_3 (0.5 M, 10 mL). The re-protonated HcOF-7 was washed with dioxane (10 mL $\times$ 3) and THF (10 mL $\times$ 3). The successful re-protonation was confirmed by FT-IR spectroscopy.

- 5 [0180] The regenerated amorphous HcOF-7 was subjected to an iodine/iodide adsorption capacity study and a low concentration iodine/iodide removal investigation. The I_2/I^- uptake of the regenerated HcOF-7 from I_2/KI solution (I_2 : 0.87 M, KI : 1.02 M) was measured as 0.88 ± 0.03 g/g, which is lower than that of as-synthesized HcOF-7 (1.39 ± 0.07 g/g). The residual iodine concentration ($\text{I}_2 + \text{I}^-$) reached 1.3 ± 0.06 ppm after soaking the
10 regenerated amorphous HcOF-7 (6 mg) in 5 ppm I_2/KI (I_2 : 3.5 ppm, I^- : 1.5 ppm) solution at 23 °C for 72 h. For comparison, the residual iodine concentration ($\text{I}_2 + \text{I}^-$) of as-synthesized HcOF-7 reached 0.22 ± 0.02 ppm.

- [0181] **$\text{I}_2 \bullet \text{HcOF-7}$ promoted NO_3^- to I^- anion exchange.** *Preparation of $\text{I}_2 \bullet \text{HcOF-7}$.* Different amounts of I_2 (0.5, 1, and 1.5 mg) were dissolved in solvent mixtures consisting of
15 MeOH/ H_2O (2.5/2.5 mL) at room temperature before the addition of HcOF-7 (5 mg). After 72 h, these solutions turned colorless, and the UV/Vis spectroscopy confirmed that iodine was completely adsorbed (Figure 45). Next, $\text{I}_2 \bullet \text{HcOF-7}$ samples were washed with MeOH/ H_2O (5/5 mL $\times$ 3) to remove any iodine stuck on the crystal surface. The I_2 uptake amounts of $\text{I}_2 \bullet \text{HcOF-7}$ were calculated as 0.1, 0.2, and 0.3 g/g, respectively.

- 20 [0182] Different amounts of KI solution (3 mL, 3.5 mM) were added to these samples, and the molar ratio of $\text{NO}_3^-:\text{I}^-$ was kept at 1:1. After 72 h, the amounts of the exchanged I^- were measured using the dual-wavelength UV/Vis spectroscopy method (Figure 46). These experiments were repeated four times. Tukey's test confirmed the honest significant differences. The results indicate that the confidence level of the differences
25 between each iodide exchange group is 99% or higher (Figure 5c). The NO_3^- to I^- exchange ratios of HcOF-7, $\text{I}_2 \bullet \text{HcOF-7}$ (0.1 g/g), $\text{I}_2 \bullet \text{HcOF-7}$ (0.2 g/g), $\text{I}_2 \bullet \text{HcOF-7}$ (0.3 g/g) are measured as 27 ± 1 %, 33 ± 2 %, 37 ± 2 %, and 39 ± 1 %, respectively.

- [0183] **Investigation of low concentration I_2/I^- removal in aqueous solutions.** *Static adsorption:* The stock solution of the I_2/I^- mixture (3.5 mg/L $\text{I}_2 + 1.5$ mg/L I^-) was
30 prepared by dissolving I_2 (3.5 mg) and KI (1.96 mg) in 1L of DI water. Based on the equilibrium constant, the concentrations of I_2 , I^- and I_3^- were calculated as 3.48, 1.49, and 0.04 ppm, respectively. Since the concentration of I_3^- is two orders of magnitude less than the concentration of I_2 , the contribution of I_3^- is negligible.

[0184] Activated HcOF-7 (6 mg) crystals were added to 3 mL of I_2/I^- solution (3.5 mg/L I_2 + 1.5 mg/L I^-) or I^- solution (1.5 mg/L) in a 4-mL vial. The samples were kept at room temperature (23 °C) or heated to desired temperatures (40, 50, 70, and 90 °C) in an oil bath. After 72 h, the total iodine residues ($I_2 + I^-$) of the solution were determined by the Leuco-crystal violet method. As a reference, CHOP-7 (10 mg) was subject to similar measurements in the I_2/I^- solution (3.5 mg/L I_2 + 1.5 mg/L I^-) at 23, 40, 50, 70 and 90 °C, respectively. The experiments were repeated three times.

[0185] **I_2/I^- removal in the presence of competing anions.** To investigate the I_2/I^- sorption in the presence of potential competing anions that simulates the natural water, NO_3^- (5 ppm), $H_2PO_4^-$ (5 ppm), SO_4^{2-} (20 ppm), Cl^- (80 ppm), HCO_3^- (60 ppm) were added to I_2/I^- solution (I_2 : 3.5 ppm, I^- : 1.5 ppm) separately. HcOF-7 crystals (6 mg) were added to these solutions (3 mL) that possess NO_3^- , $H_2PO_4^-$, SO_4^{2-} , Cl^- , and HCO_3^- , respectively. In addition, a mixture of NO_3^- , $H_2PO_4^-$, SO_4^{2-} , Cl^- , and HCO_3^- iodinated solution (3 mL) with the same concentrations mentioned above was prepared for iodine removal. After 72 h, the total iodine residue concentrations were measured as 0.30 ± 0.02 , 0.27 ± 0.01 , 0.32 ± 0.02 , 0.38 ± 0.03 , 0.43 ± 0.03 , 0.46 ± 0.02 ppm, respectively by the Leuco-crystal violet method.

[0186] **Breakthrough experiments.**

[0187] **HcOF-7 column preparation.** HcOF-7 crystals (240 mg) were exchanged by THF (5×30 mL) and hexanes (5×30 mL) for 24 h, respectively. Then HcOF-7 crystals and hexanes (10 mL) were distributed evenly into a ball-milling steel container with 3 ZrO_2 balls. After grinding by ball-milling at 50 Hz for 3 minutes, the crystals were filled into a plastic syringe (length: 27 mm, inner diameter: 4.5 mm). Both ends of the syringe are blocked with cotton. Before the iodine adsorption experiment, THF (30 mL) was passed through into the column to make the adsorbents close-packed.

[0188] **Activated carbon and [activated carbon + resin] mixed-bed column preparation.** Activated carbon (240 mg, Millipore Sigma) was ball-milled and activated at 120 °C for 24 h before use. Then, it was filled into a column (d: 4.5×1 : 26 mm), with both ends capped by cotton. Before the breakthrough experiment, distilled water (50 mL) was passed through the column.

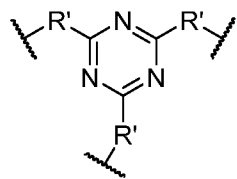
[0189] The anion exchange resin (130 mg, Dowex 1X2, 50-100 mesh) is immersed in the distilled water for 6 h before use. Then, the resin and activated carbon (130 mg) was packed into a column (d: 4.5×1 : 30 mm), with both ends capped by cotton. Before the breakthrough experiment, distilled water (50 mL) was passed through the column.

[0190] Temperature-controlled breakthrough experiment. The breakthrough experiment setup is shown in Figure 5. Iodine solution (I_2 : 3.5 mg/L and I^- : 1.5 mg/L) was prepared in a plastic bottle (4 L). A steel cartridge (300 mL) with the heating tape covered was connected to the entrance of the column. The flow rate was controlled at 5 mL/min. The temperature was adjusted by controlling the voltage of the heating tape. After the temperature was stabilized, the HcOF-7 column was installed. The iodine solution passed through the HcOF-7 column and was collected into the test tubes. The residual concentration of $[I_2 + I^-]$ of the collected solution after the column was determined by the Leuco-crystal violet method (Figure 5e).

[0191] Although the present disclosure has been described with respect to one or more particular embodiments and/or examples, it will be understood that other embodiments and/or examples of the present disclosure may be made without departing from the scope of the present disclosure.

CLAIMS:

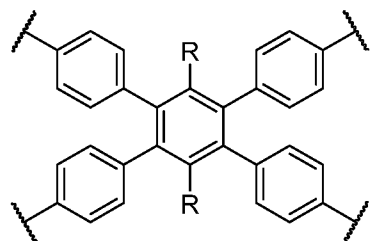
1. An organic framework comprising a plurality of linked monomers comprising one or more



(“A group”), wherein R' is –NH– or –O–, and the organic framework is at least 95%

5 crystalline.

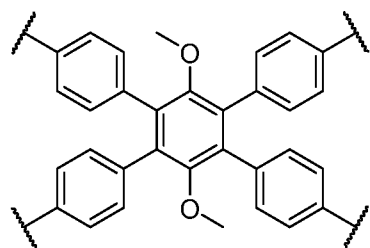
2. The organic framework according to claim 1, wherein the monomers further comprise:



(“B group”), wherein each R is individually chosen from hydrogen, methoxy groups, ethoxy groups, alkoxy groups, alkylamino groups, alkyl ester groups, and alkyl groups; and each B group is covalently bonded to one or more A group.

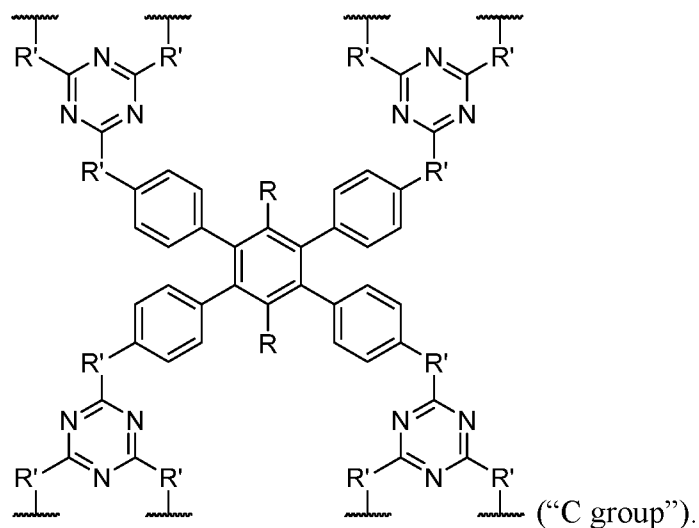
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3. The organic framework according to claim 2, wherein the B group has the following structure:

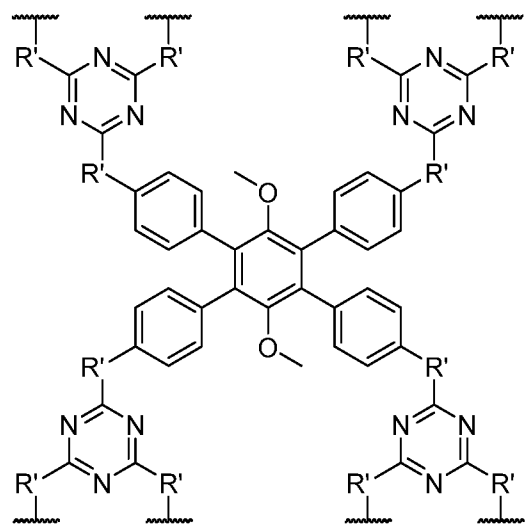


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4. The organic framework according to claim 3, comprising:

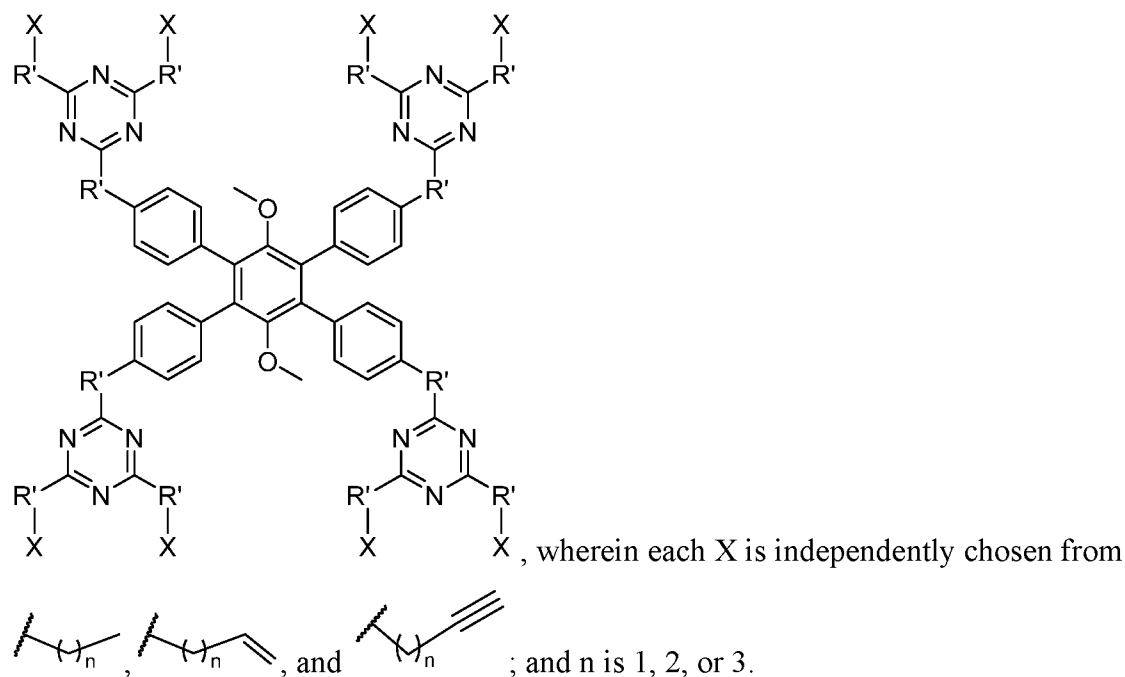


5. The organic framework according to claim 4, comprising:

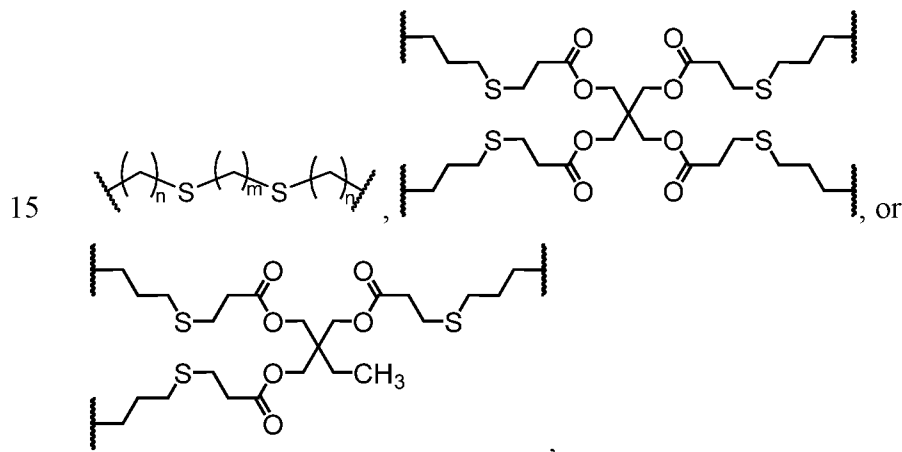


6. The organic framework according to claim 5, wherein the C groups are connected to other C groups via a crosslinking group.

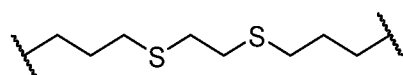
10 7. The organic framework according to claim 5, comprising:



8. The organic framework according to claim 7, wherein the monomers are crosslinked via NO_3^- ions.
9. The organic framework according to claim 6, wherein the crosslinked C groups have NO_3^- bound thereto.
10. The organic framework according to claim 6, wherein the crosslinked C groups have I_2 and/or I^- and/or I_3^- bound thereto.
11. The organic framework according to claim 6, wherein the crosslinking group has the following structure:



12. The organic framework according to claim 11, wherein the crosslinking group has the following structure:



5

13. The organic framework according to claim 1, wherein the organic framework defines one or more apertures.

14. The organic framework according to claim 13, wherein the aperture has a longest linear dimension of 3–15 Å.

10

15. The organic framework according to claim 13, wherein the aperture is 6 Å x 12 Å.

16. An article of manufacture comprising an organic framework according to claim 1.

15

17. The article of manufacture according to claim 16, wherein the article is a vessel, a column, a centrifuge tube, a filter, a fritted funnel, a syringe, or a filtration membrane.

18. A method for removing I₂ and/or I⁻ comprising contacting a medium comprising I₂ and/or I⁻ with an organic framework according to claim 1.

20

19. The method according to claim 18, wherein the medium is water.

20. The method according to claim 18, wherein the organic framework is a plurality of single crystals.

25

21. The method according to claim 18, wherein an article comprises the organic framework or the organic framework is disposed on a surface of the article.

22. The method according to 18, wherein the contacting is performed at a temperature greater than room temperature.

30

23. The method according to claim 22, wherein the temperature is at least 90 °C.

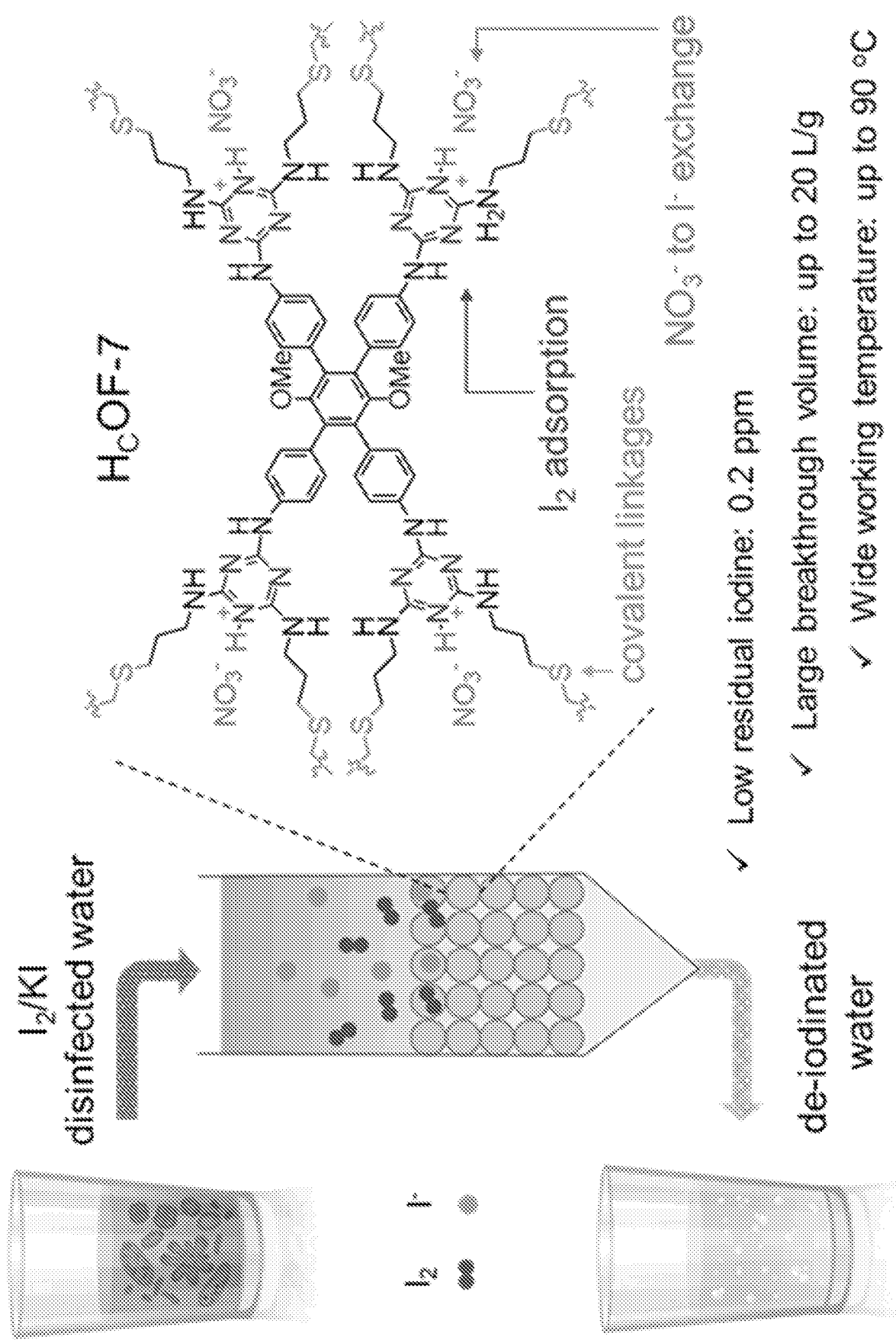


Figure 1

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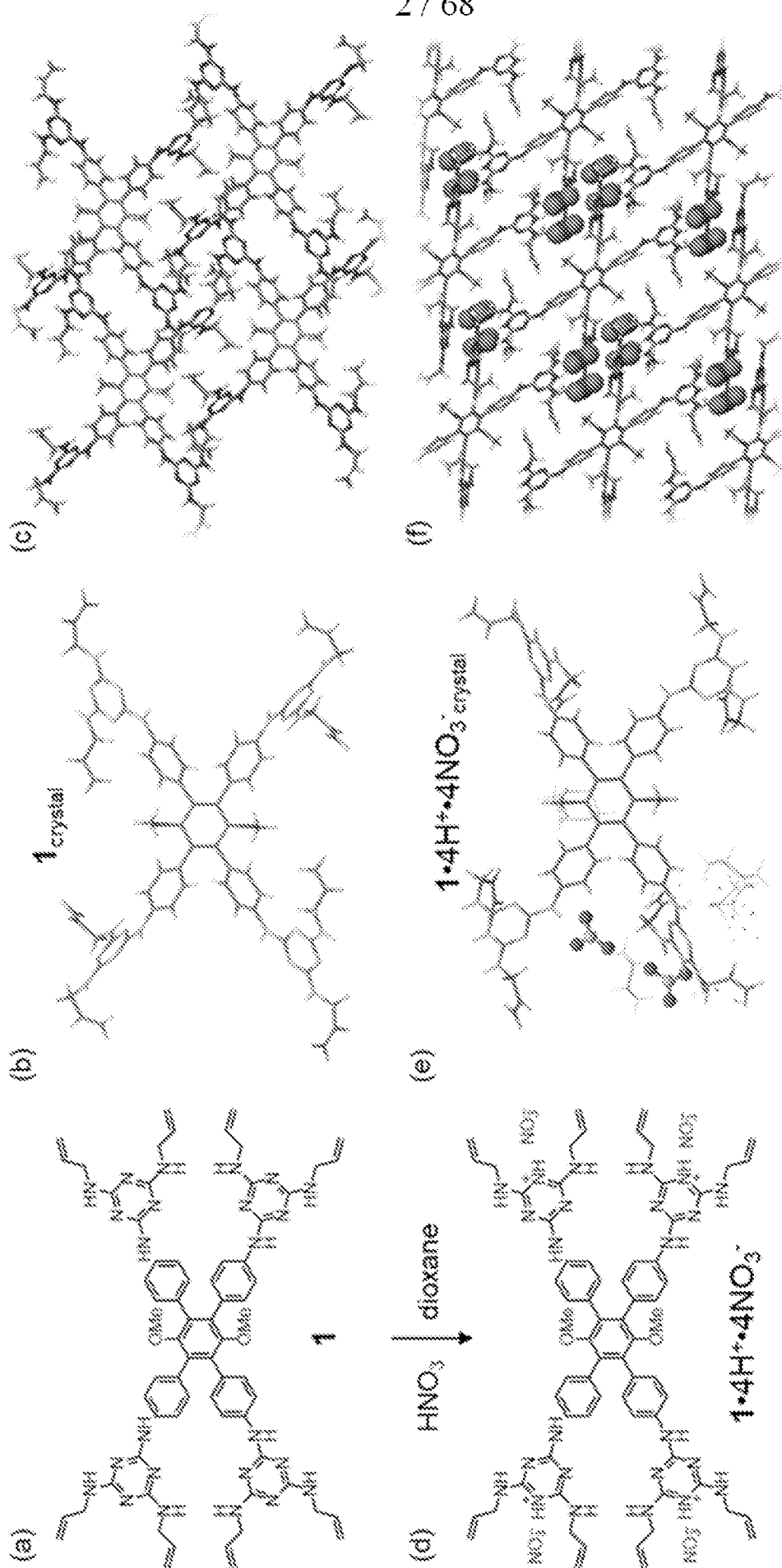


Figure 2

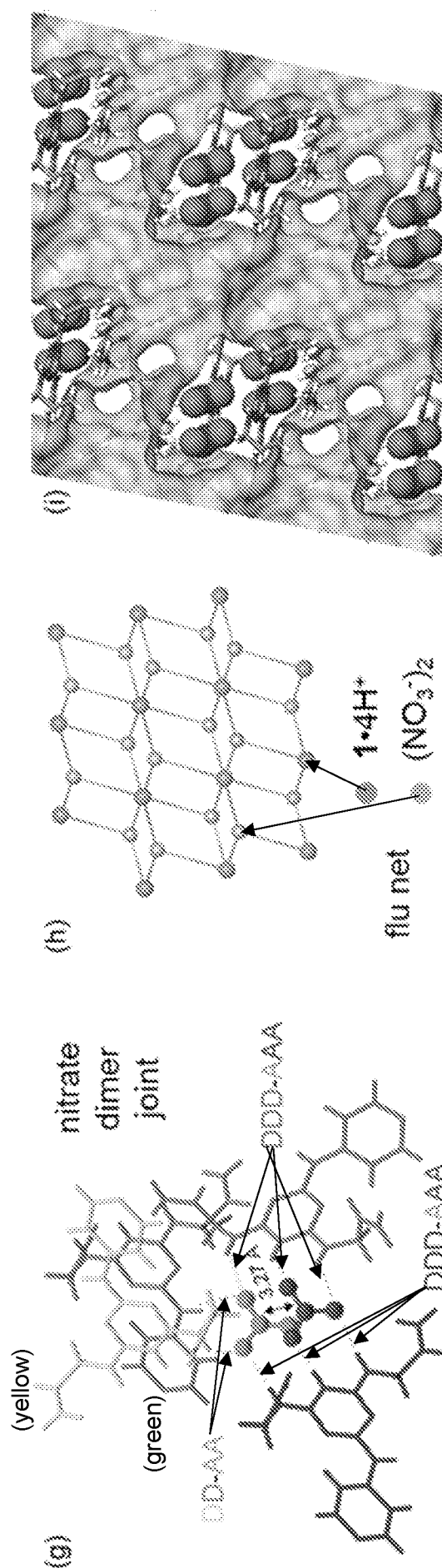


Figure 2 (continued)

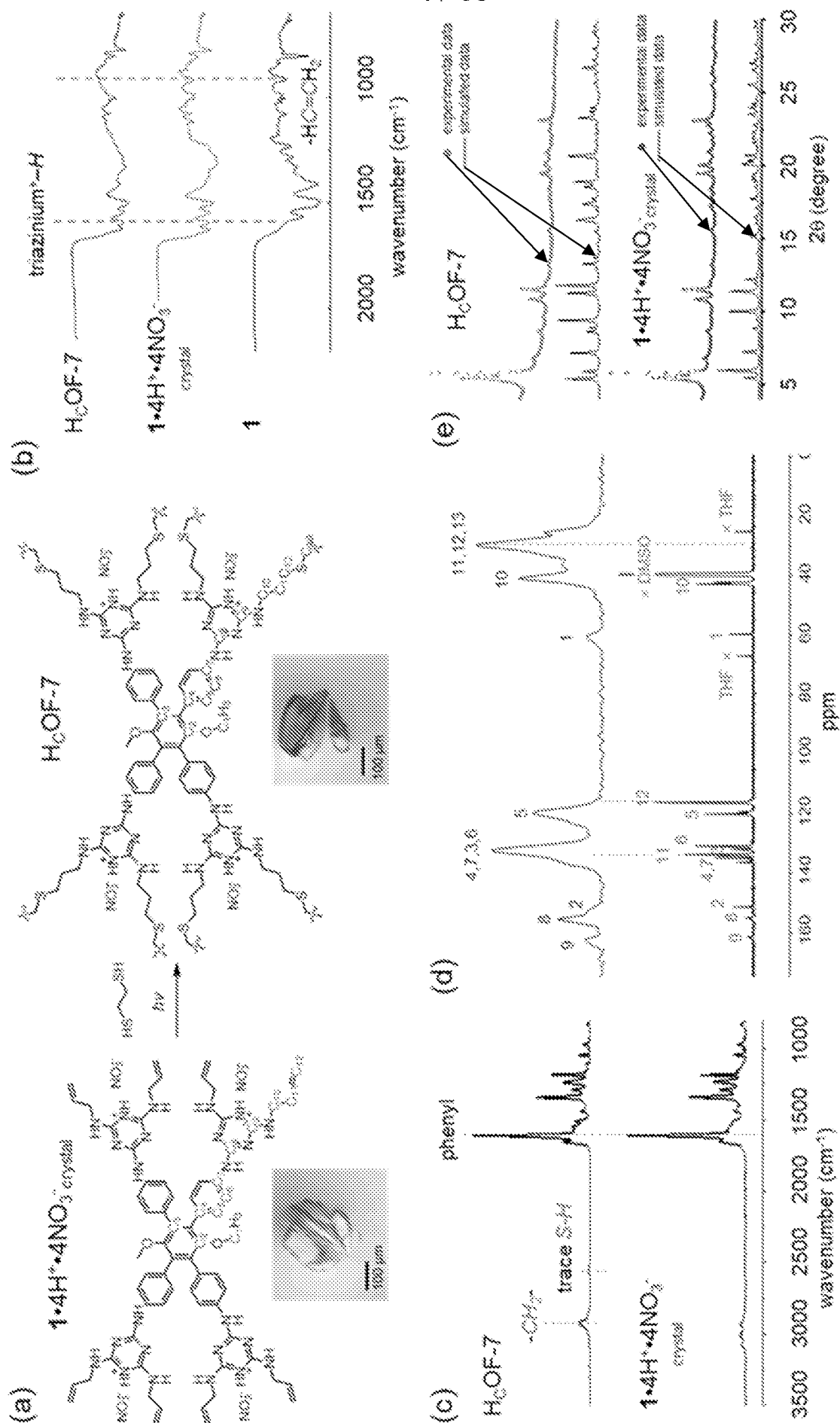


Figure 3

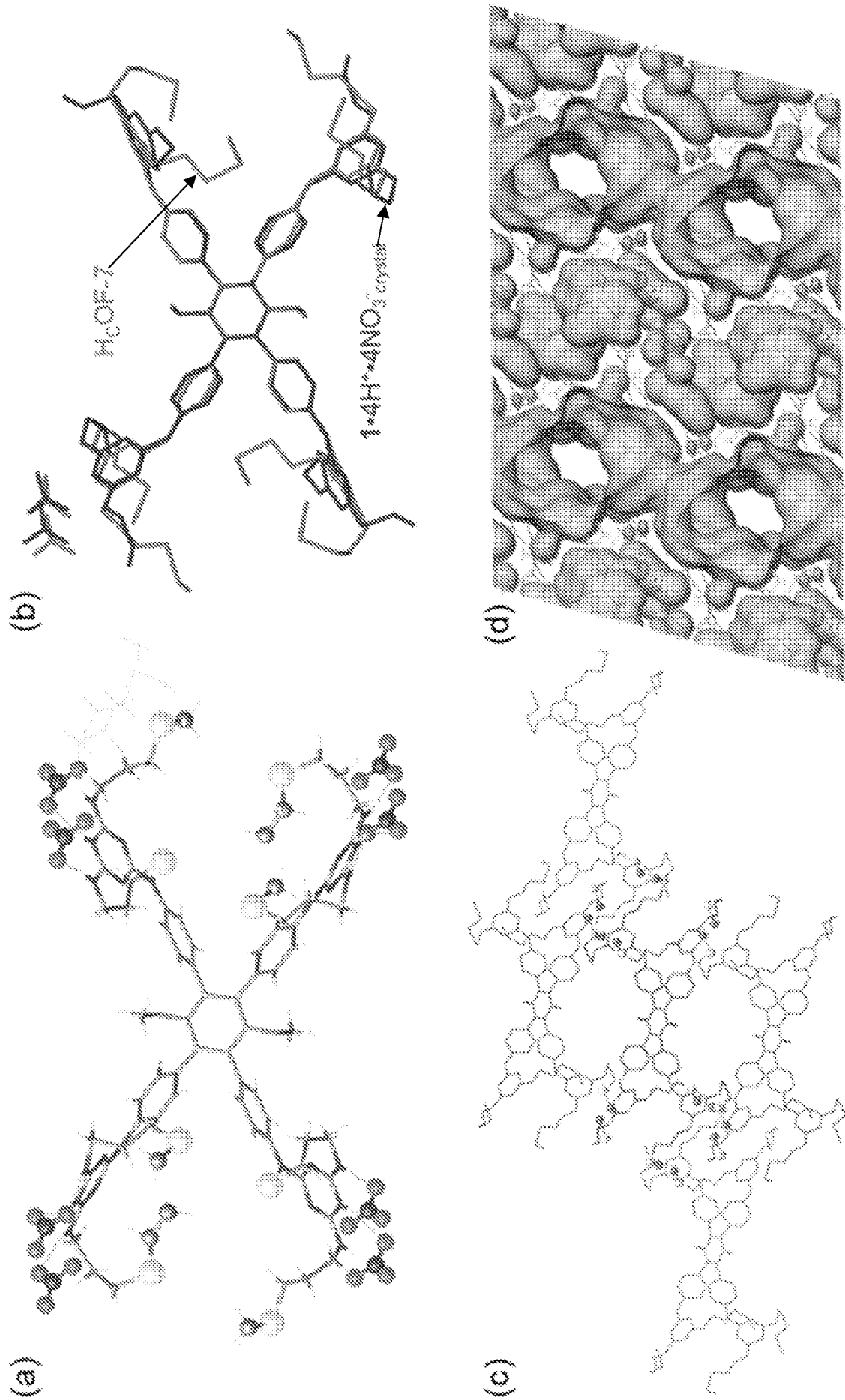


Figure 4

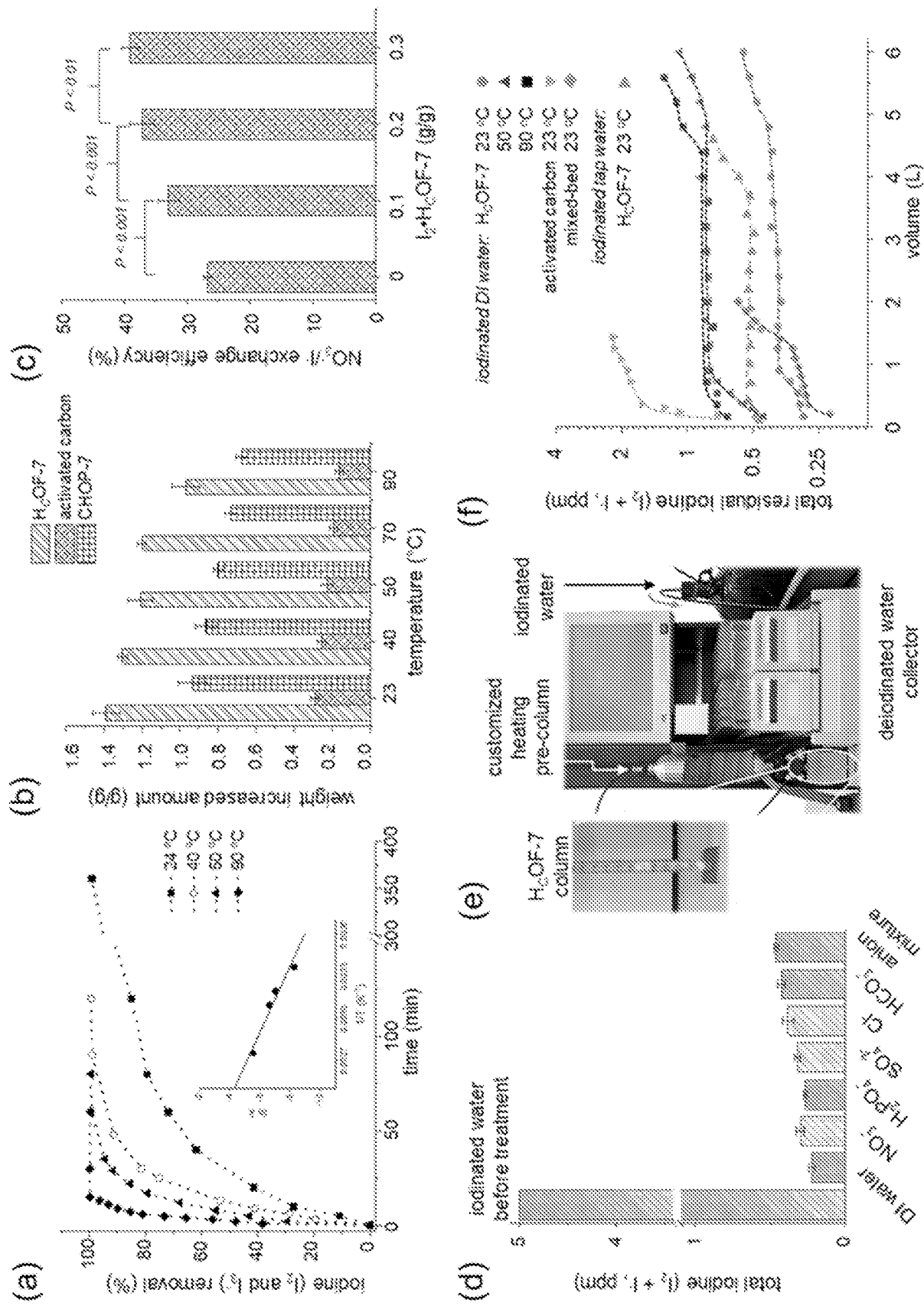


Figure 5

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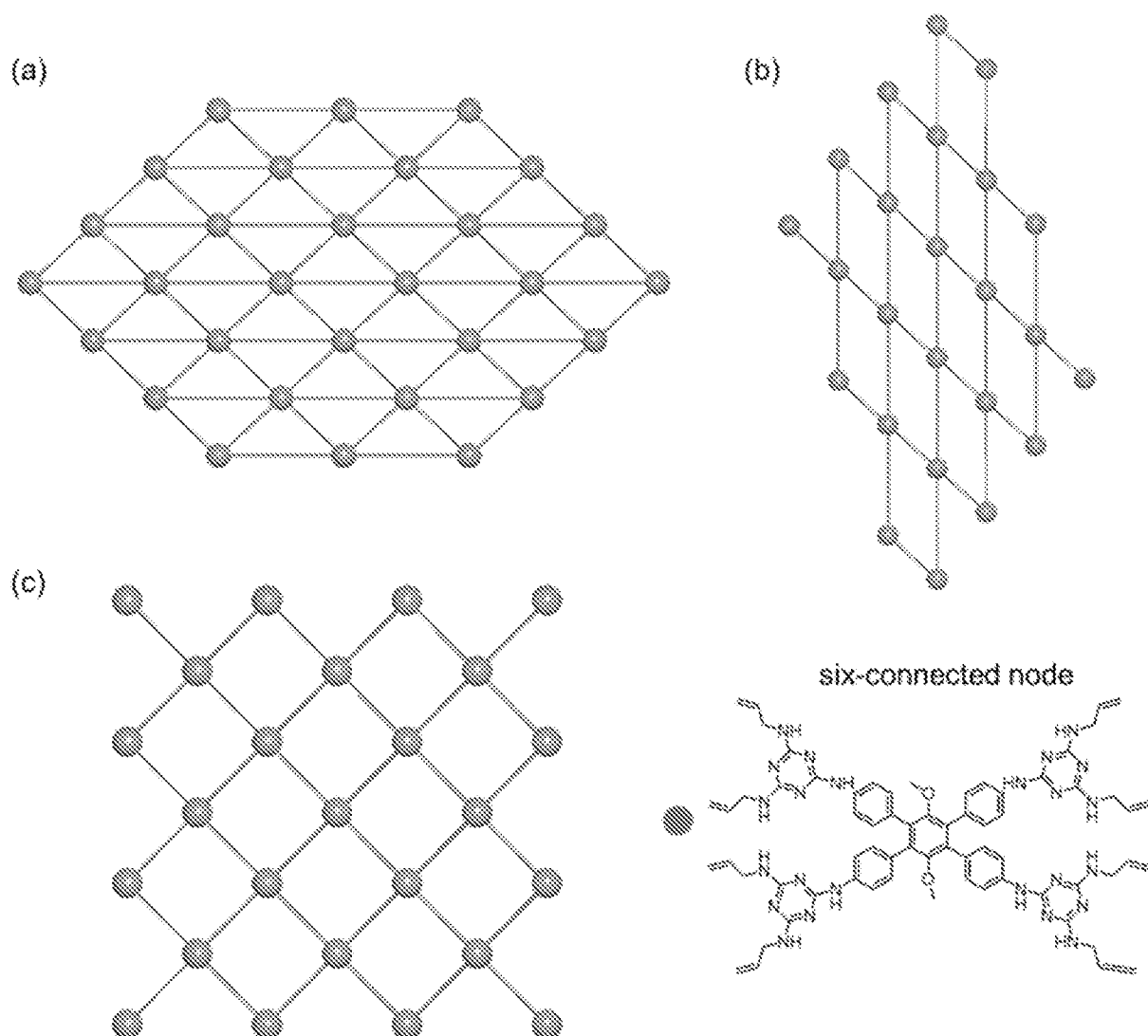


Figure 6

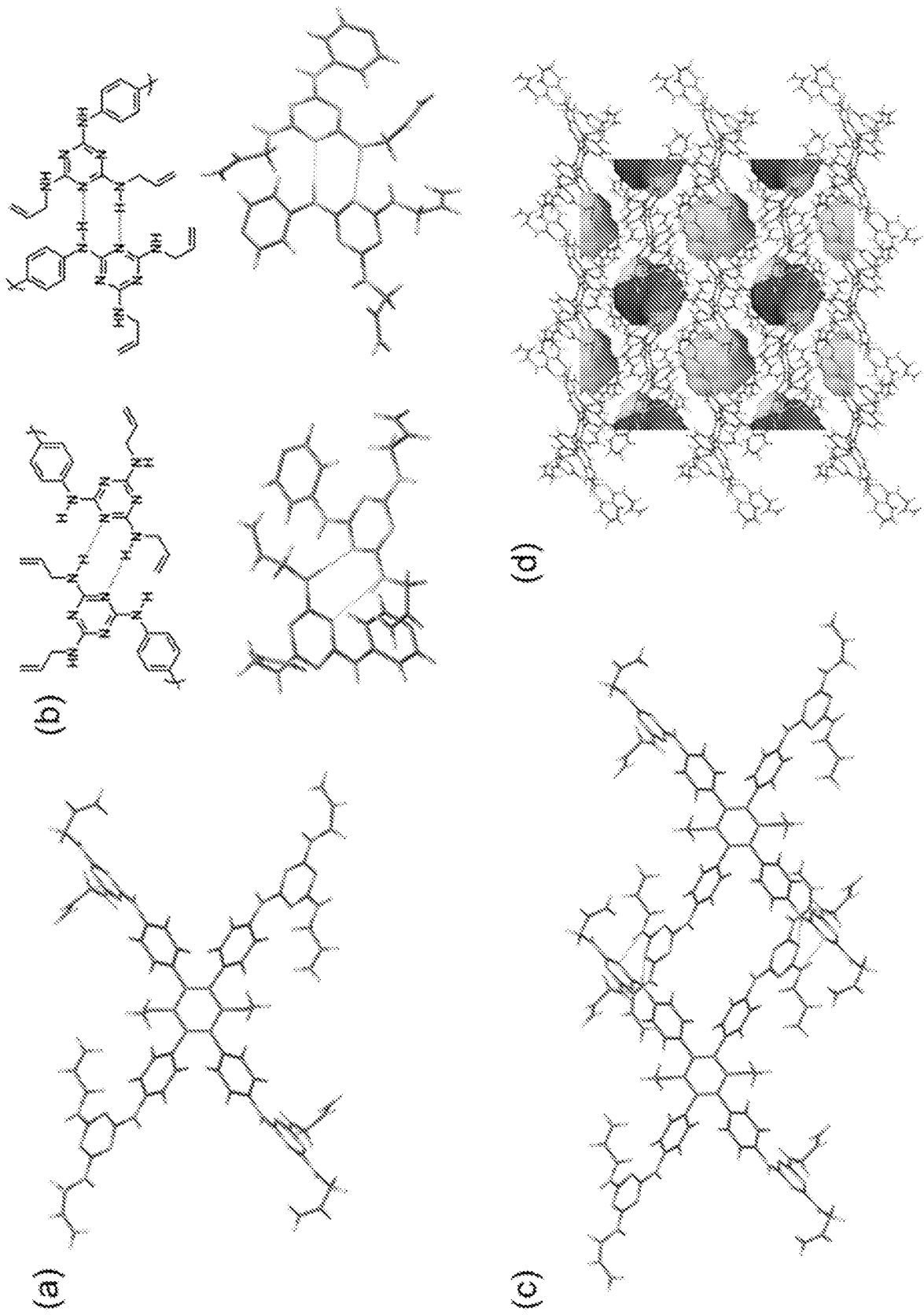


Figure 7

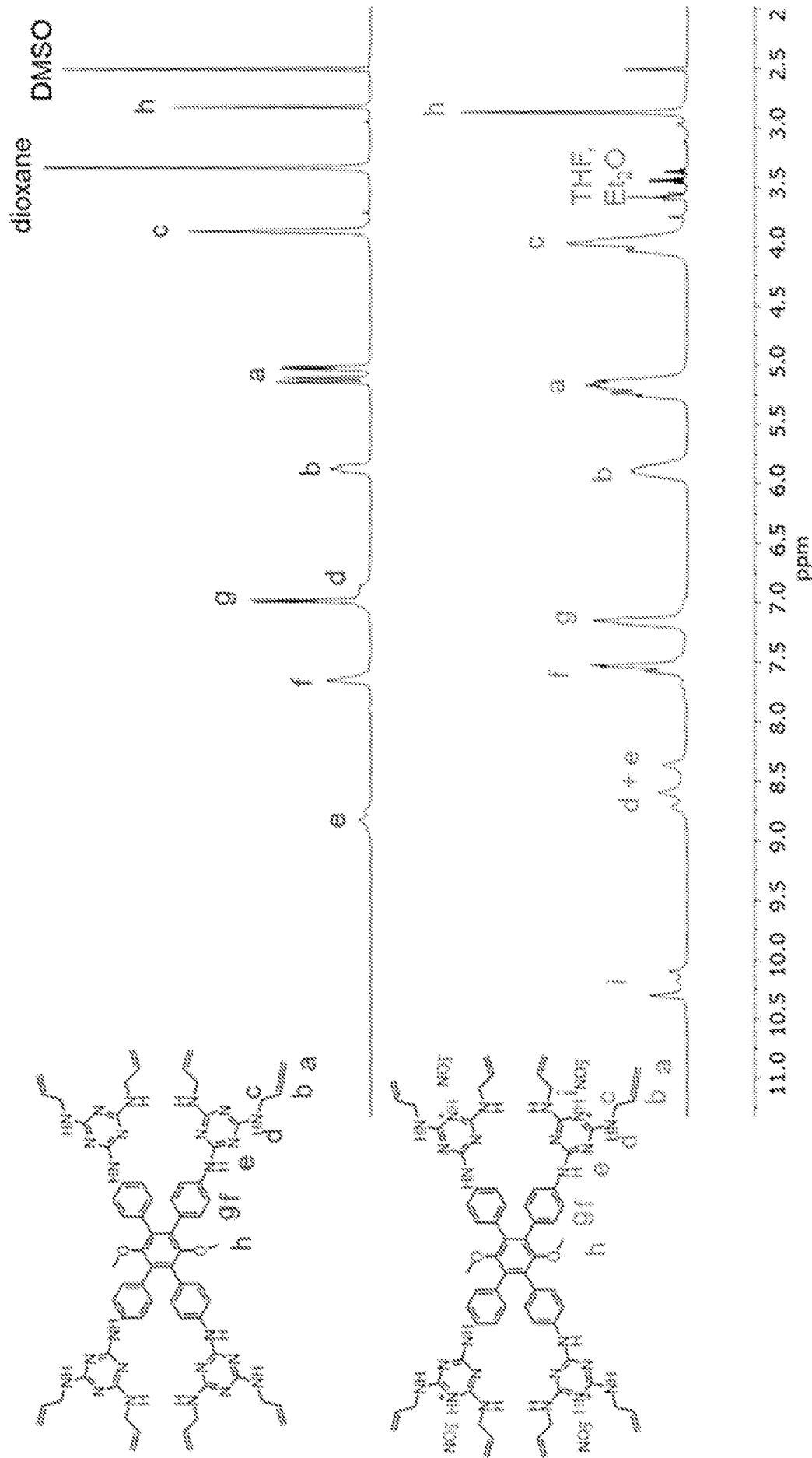


Figure 8

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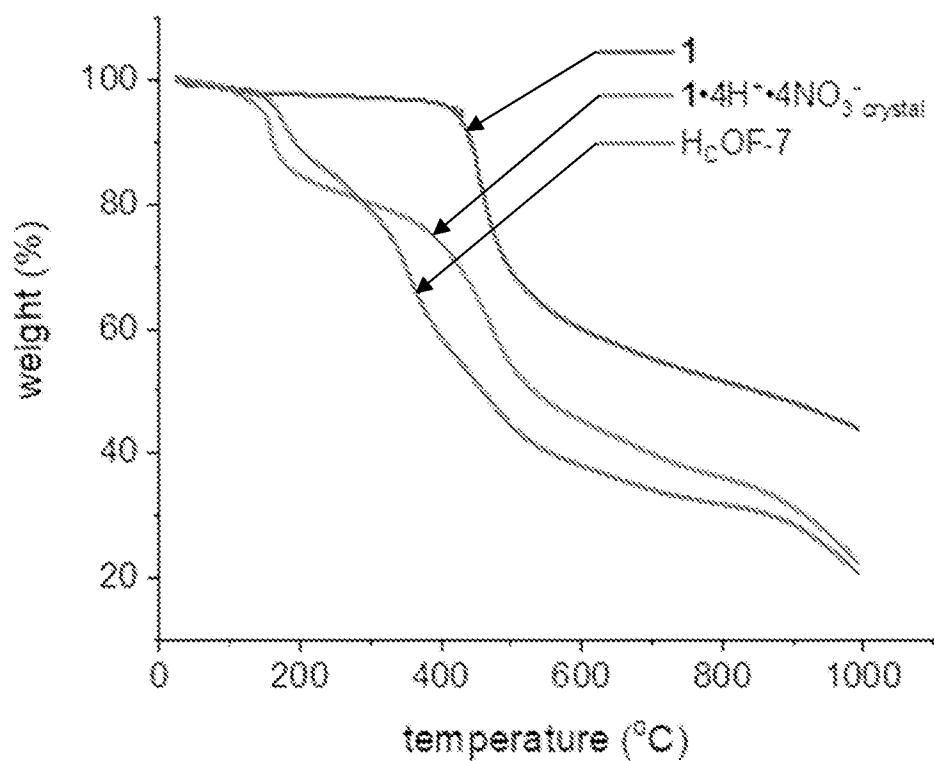


Figure 9

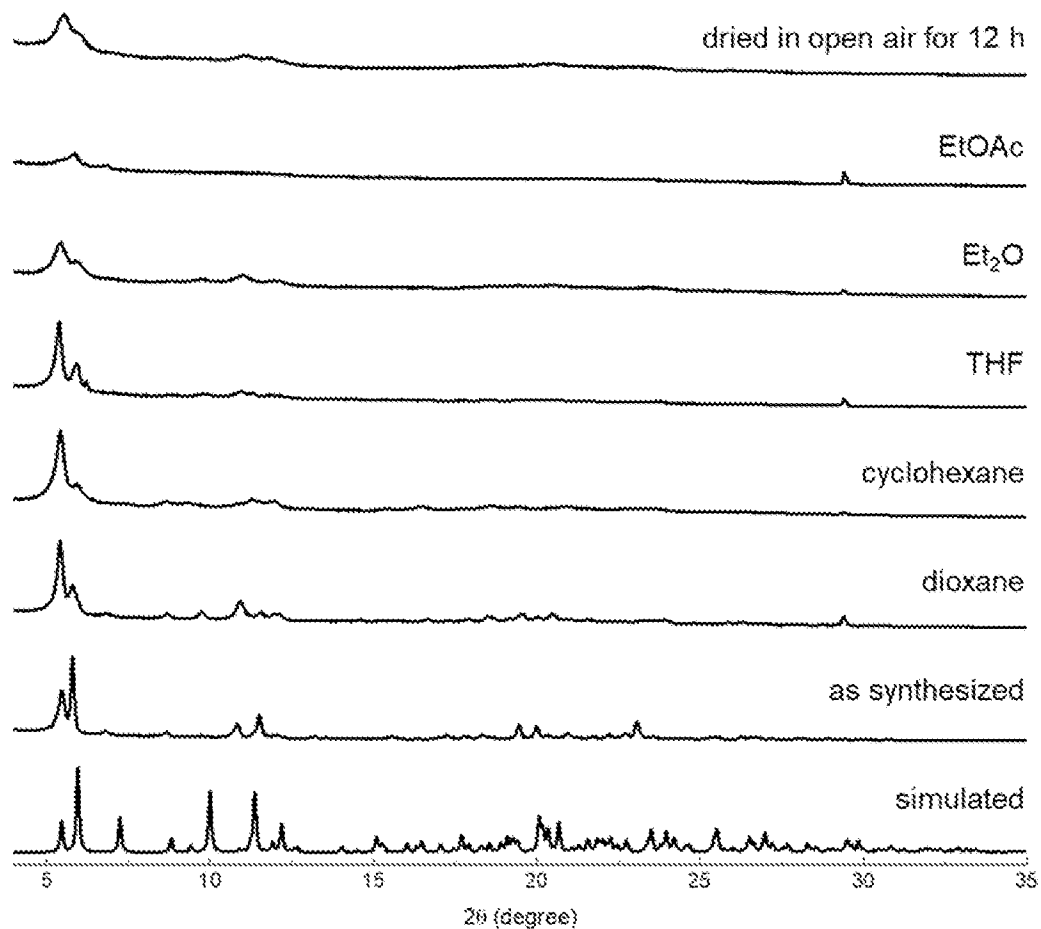


Figure 10

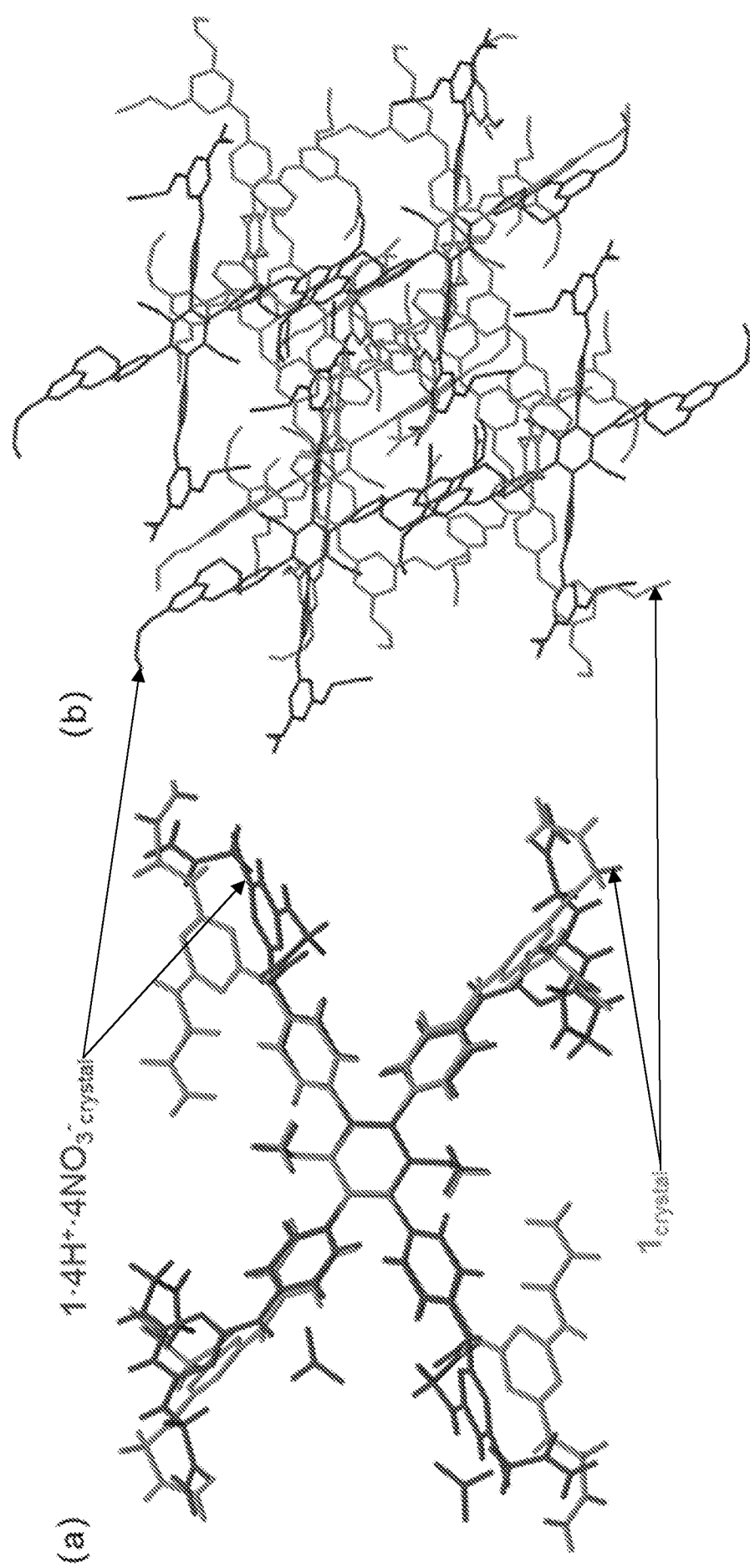


Figure 11

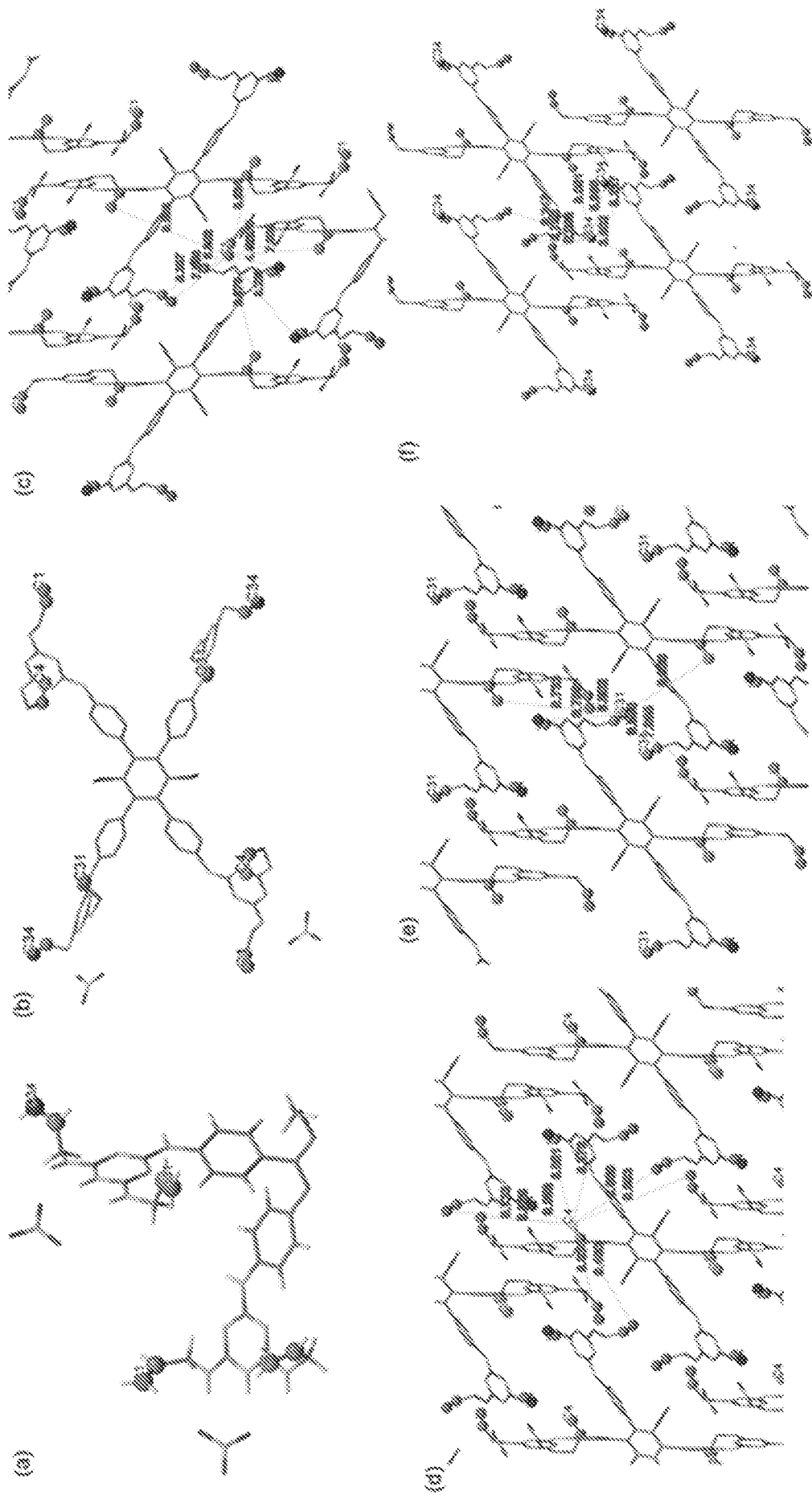


Figure 12

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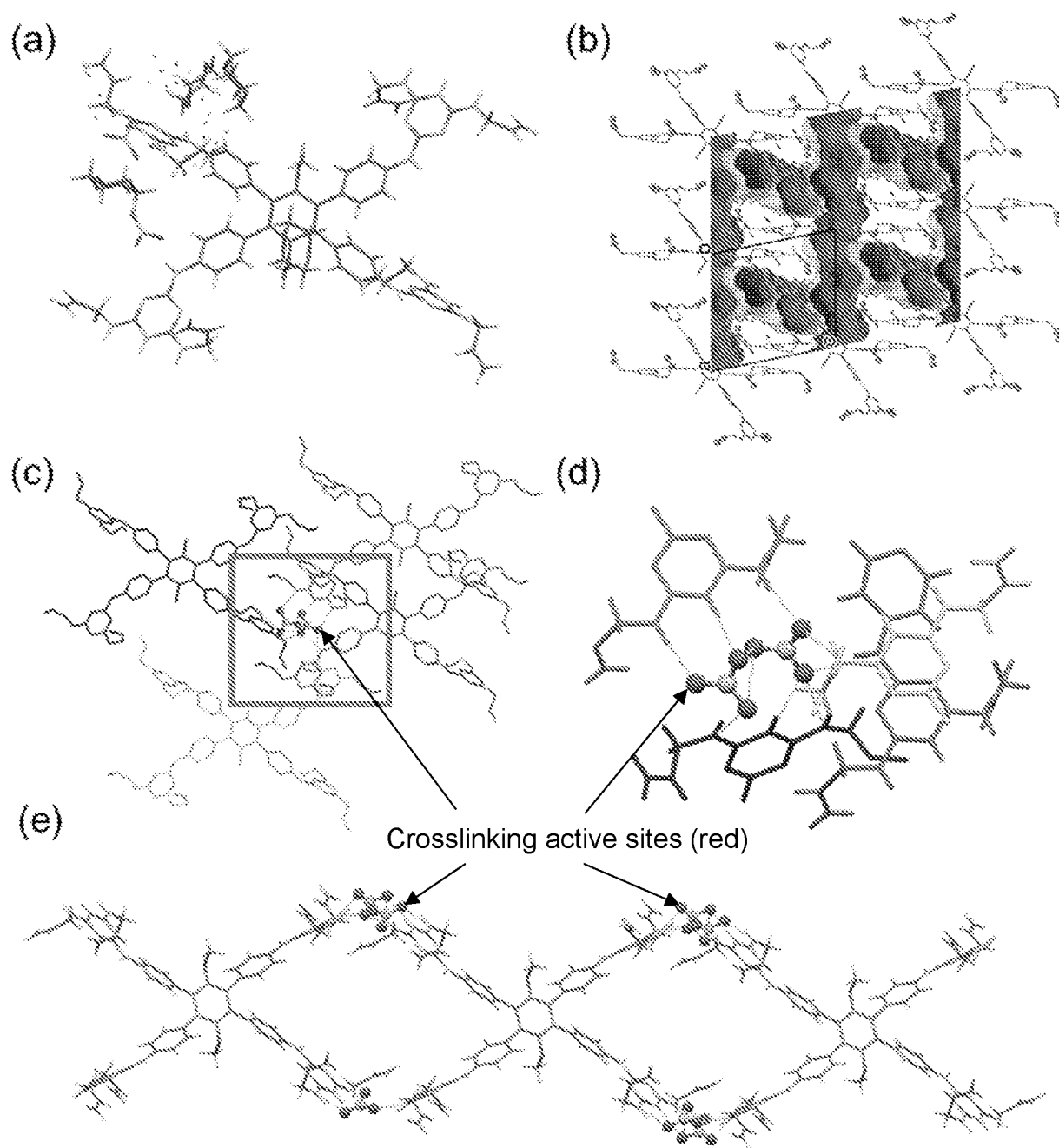


Figure 13

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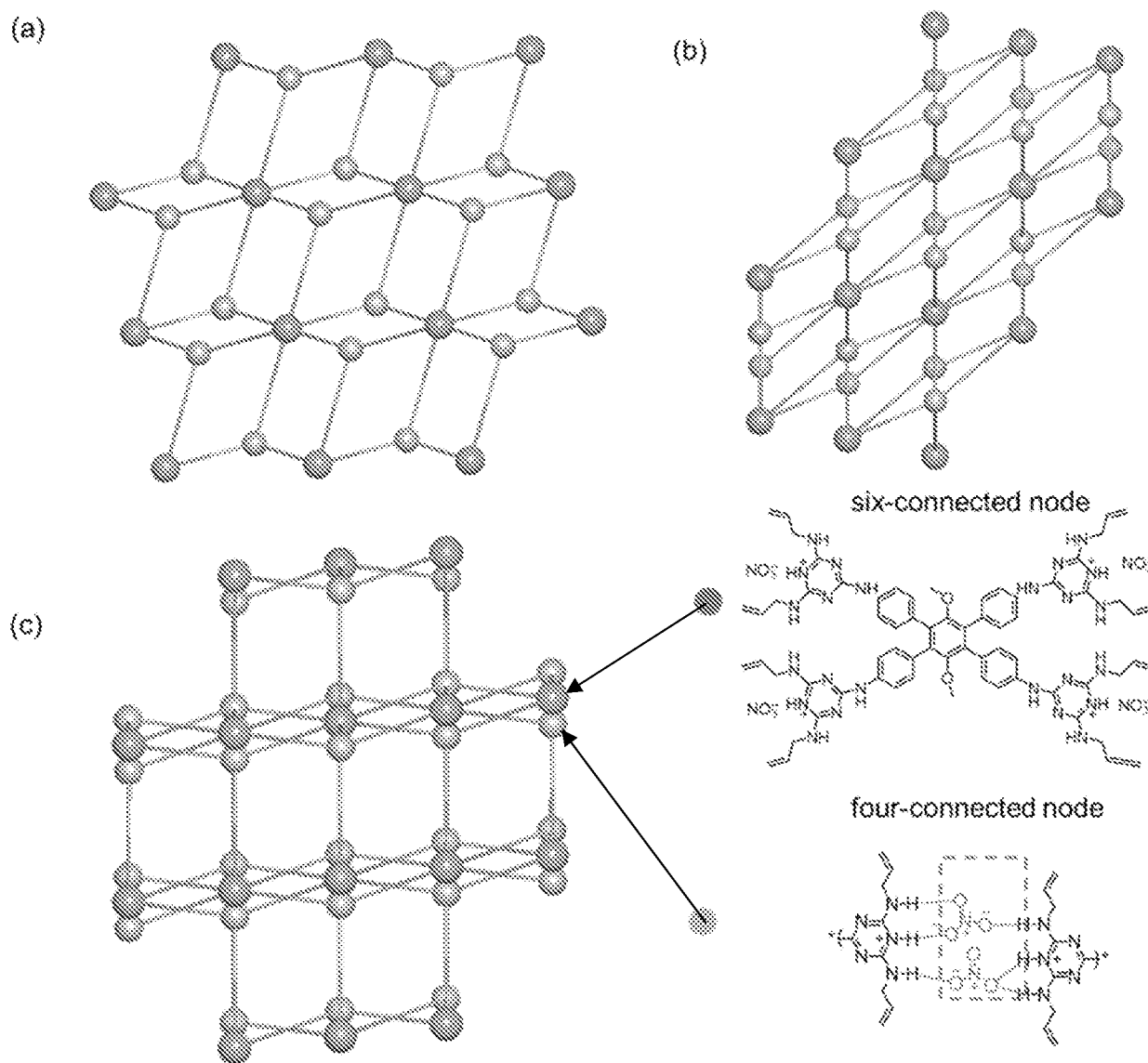


Figure 14

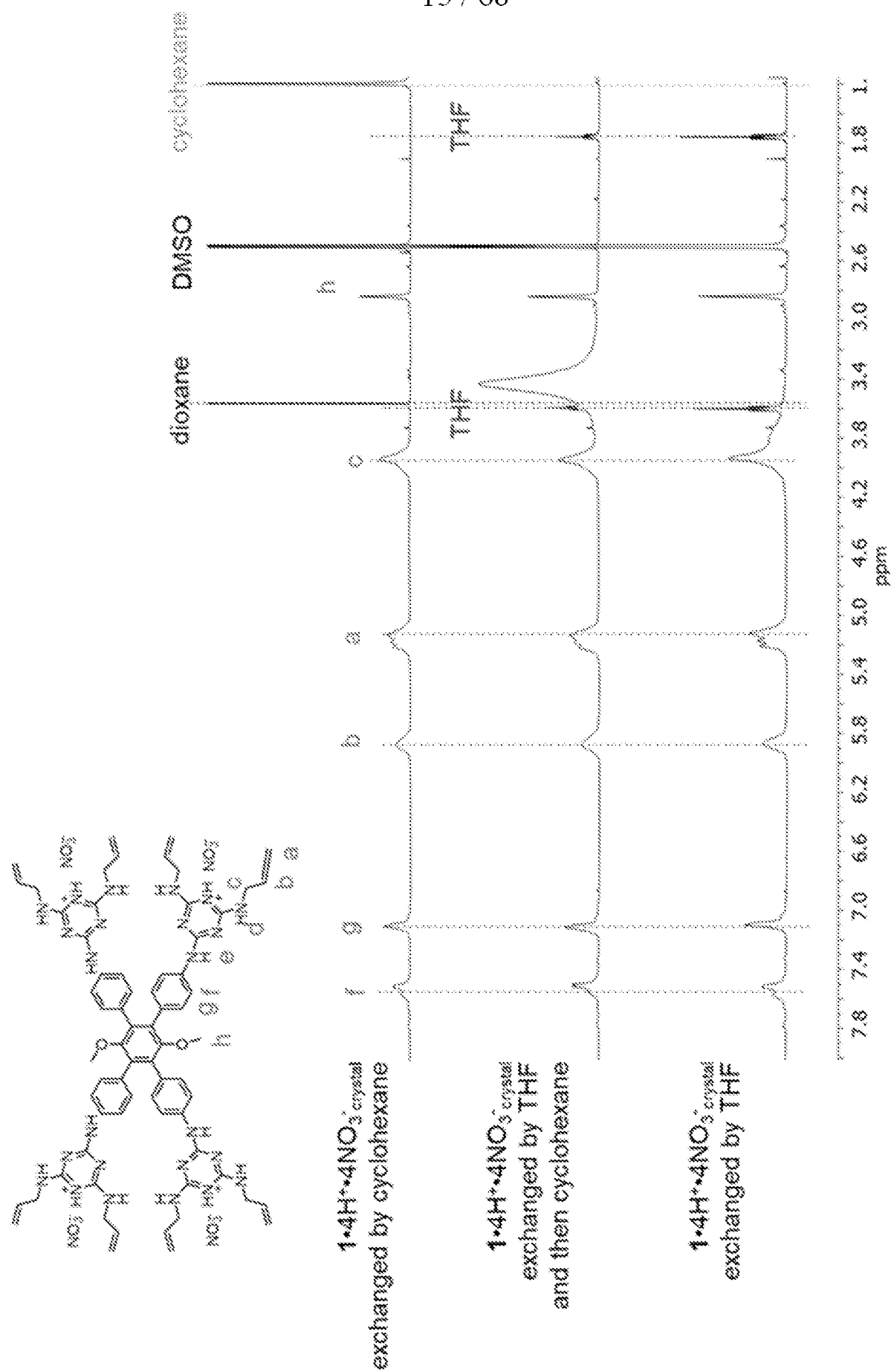


Figure 15

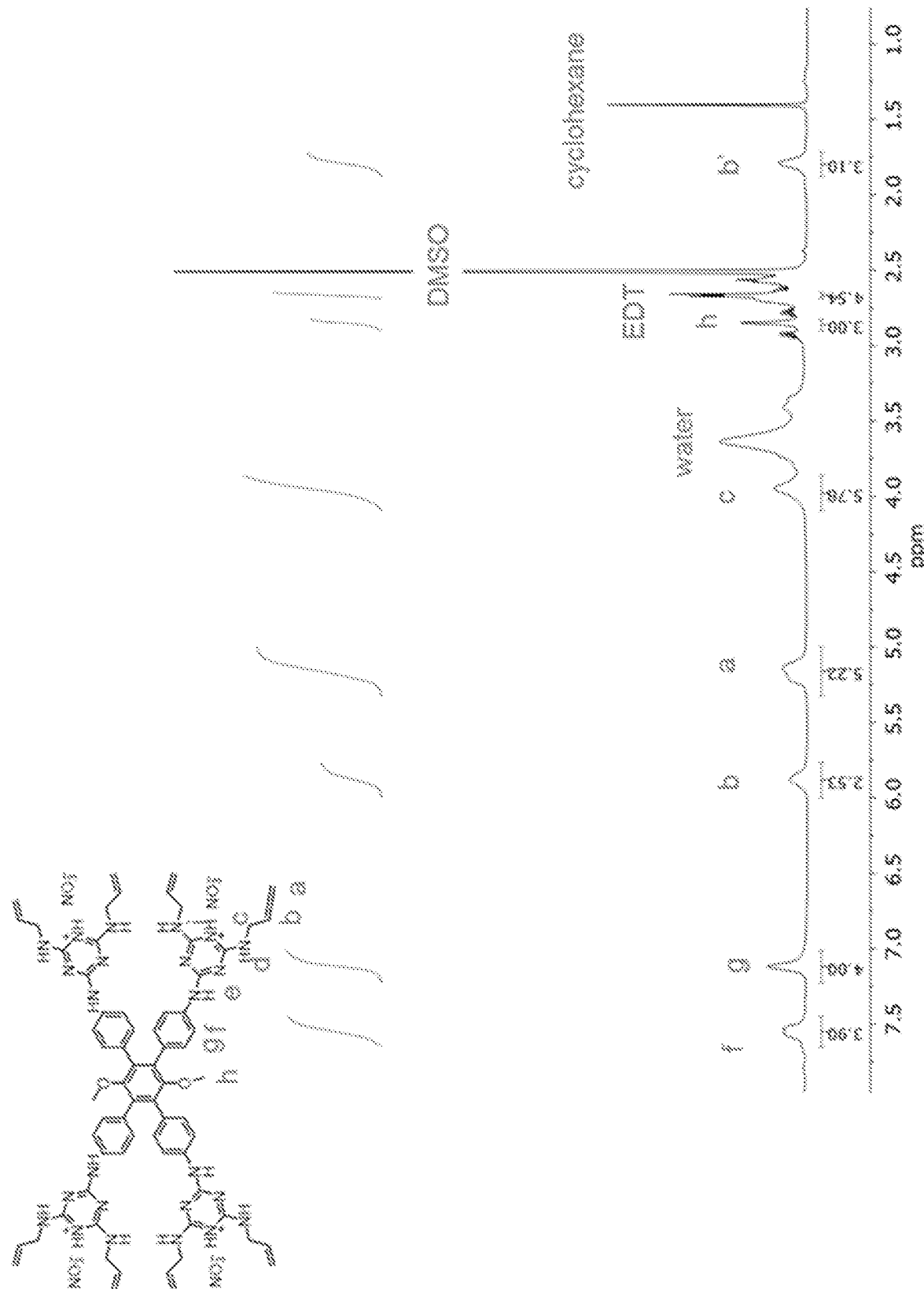


Figure 16

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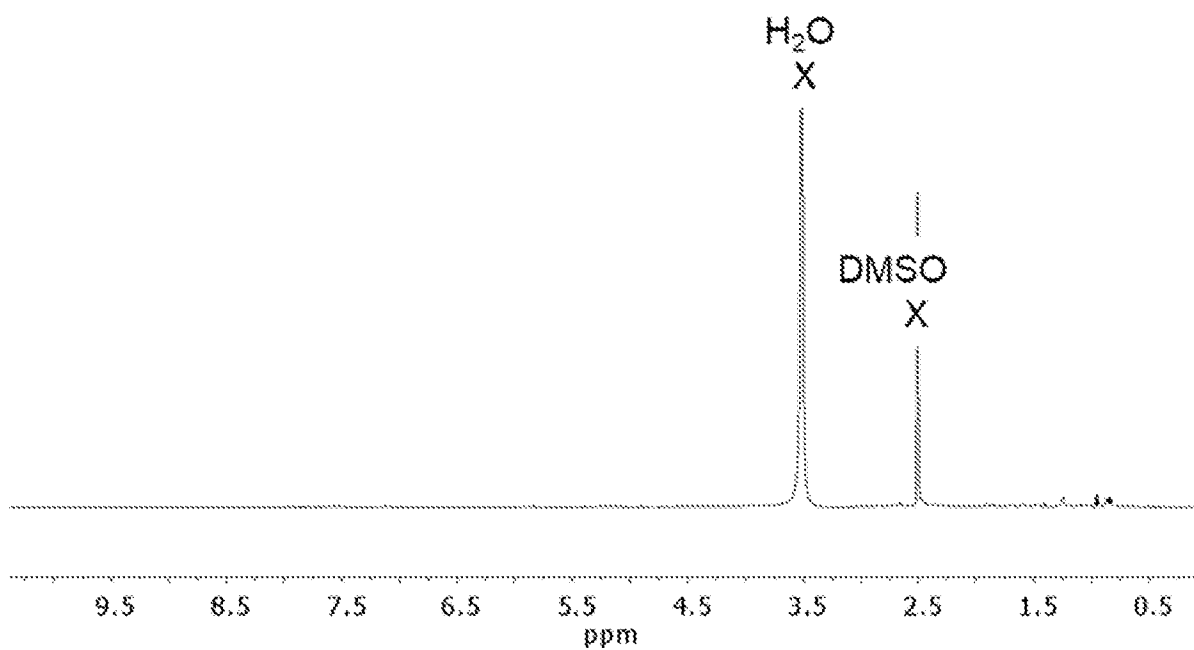


Figure 17

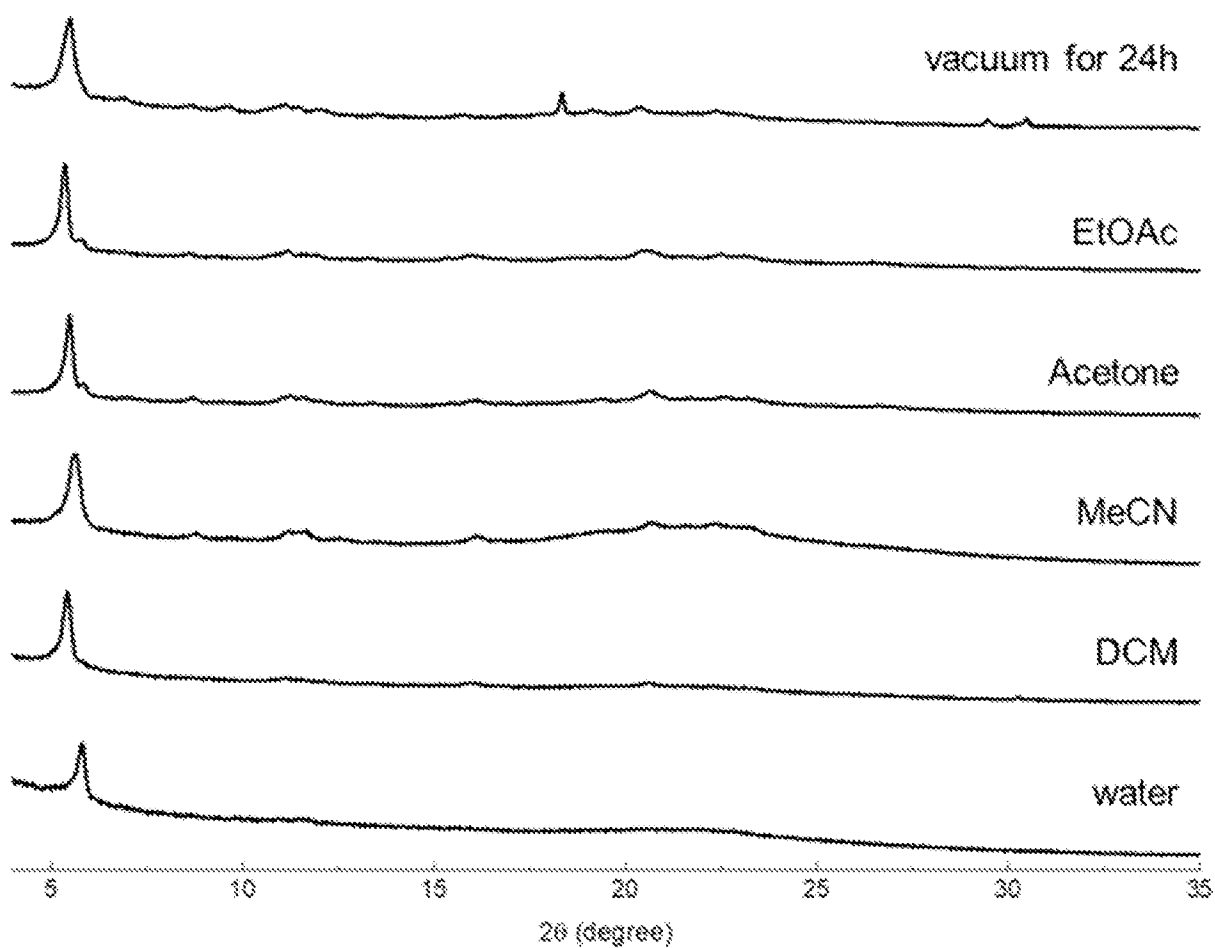


Figure 18

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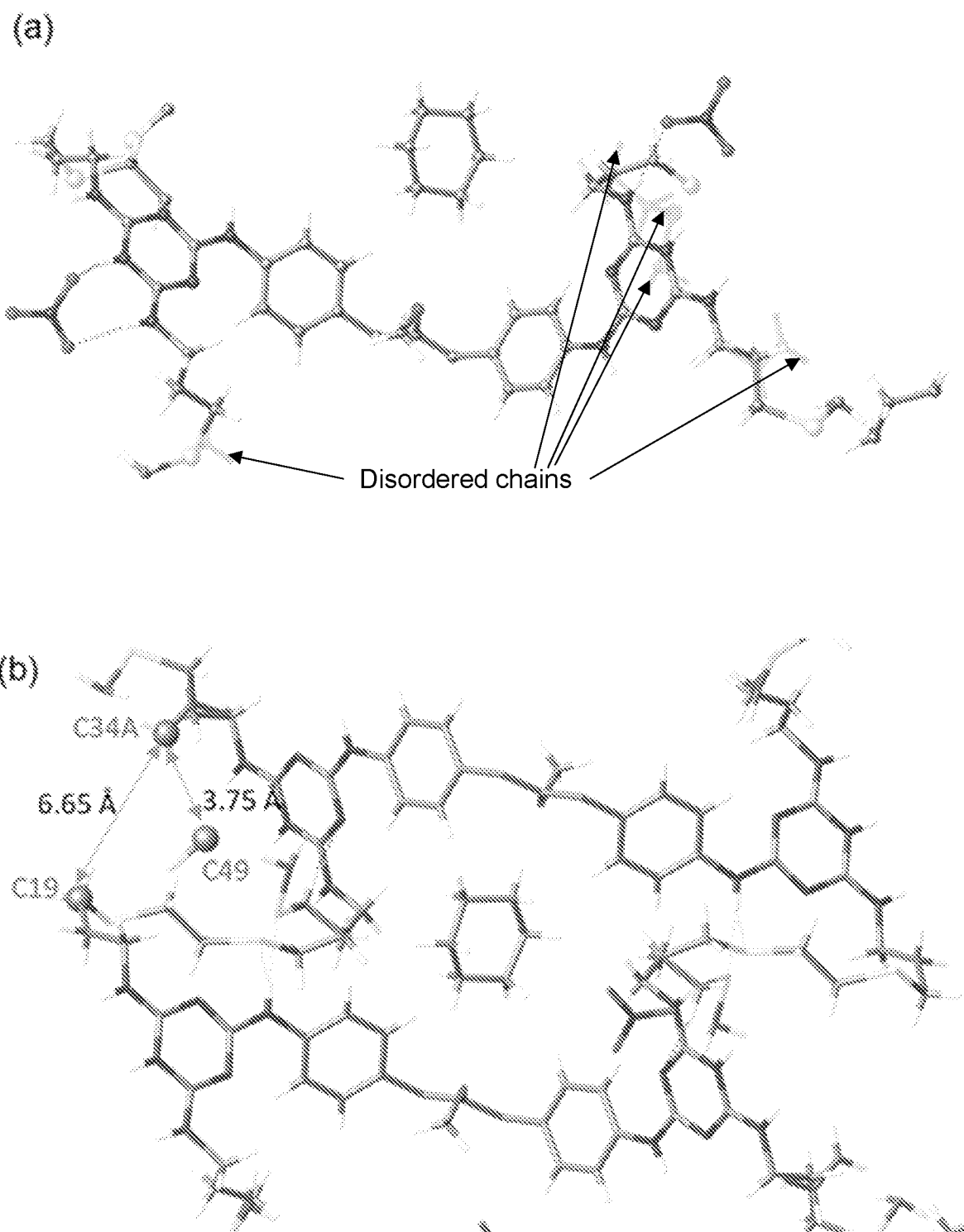


Figure 19

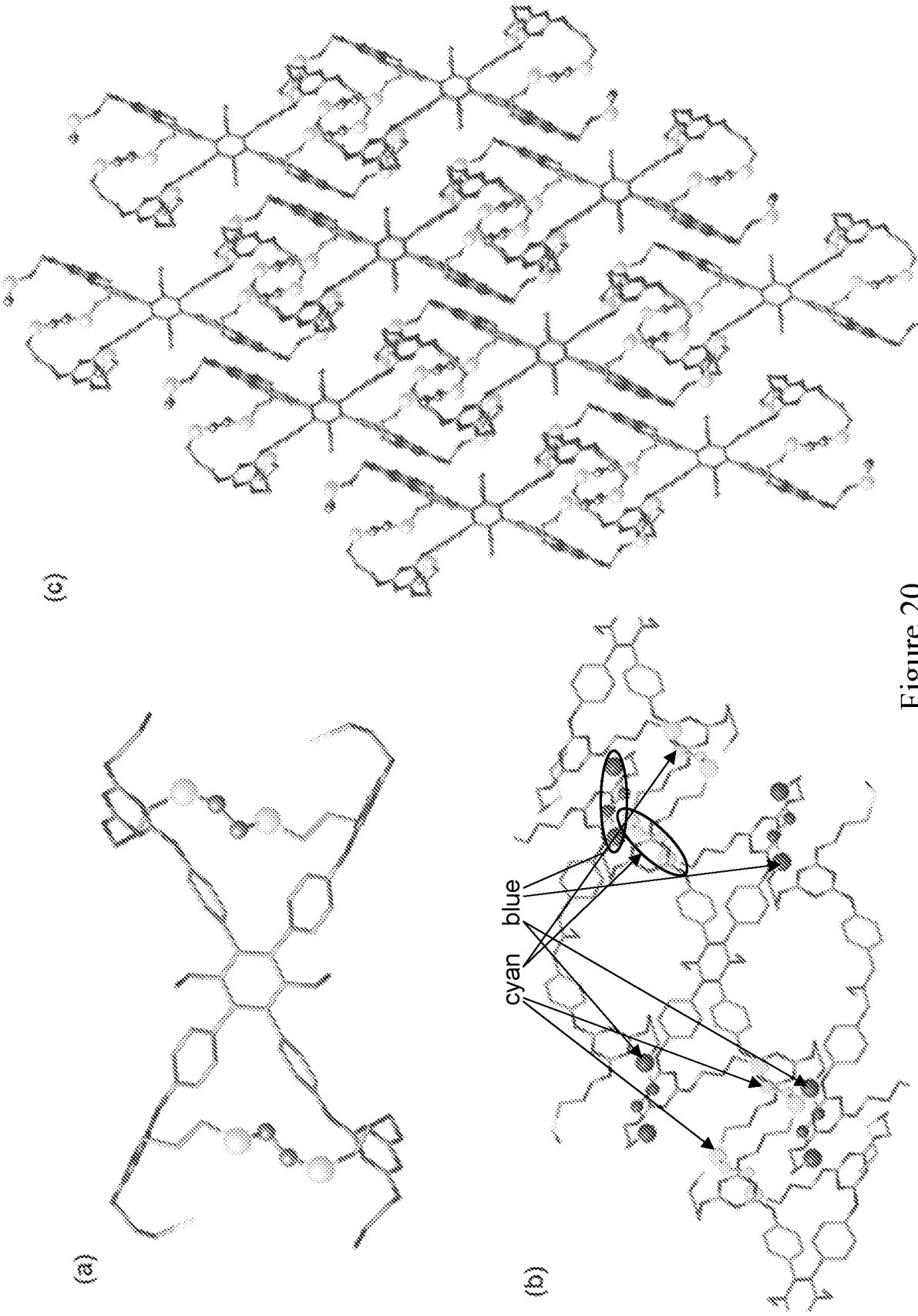


Figure 20

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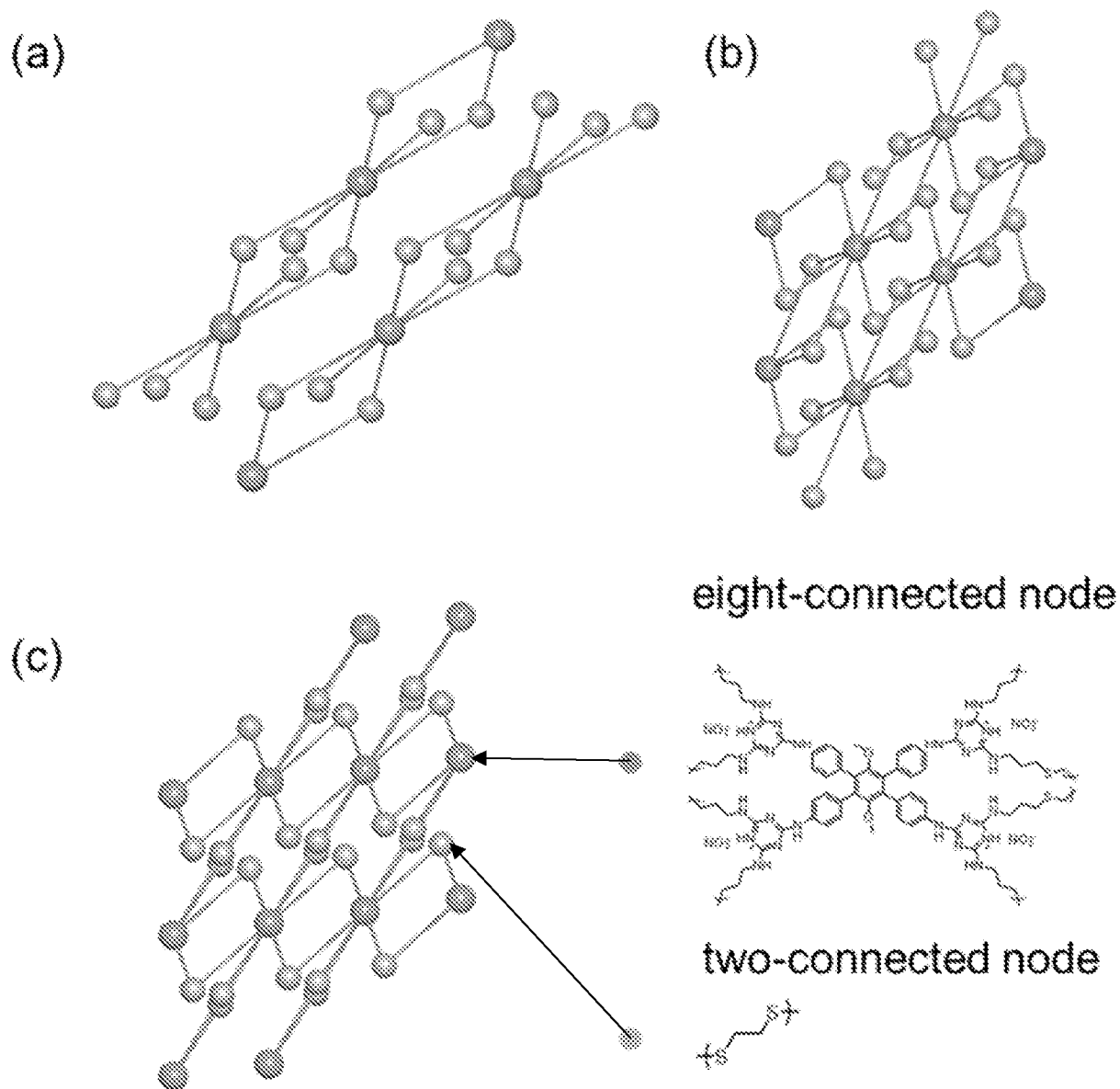


Figure 21

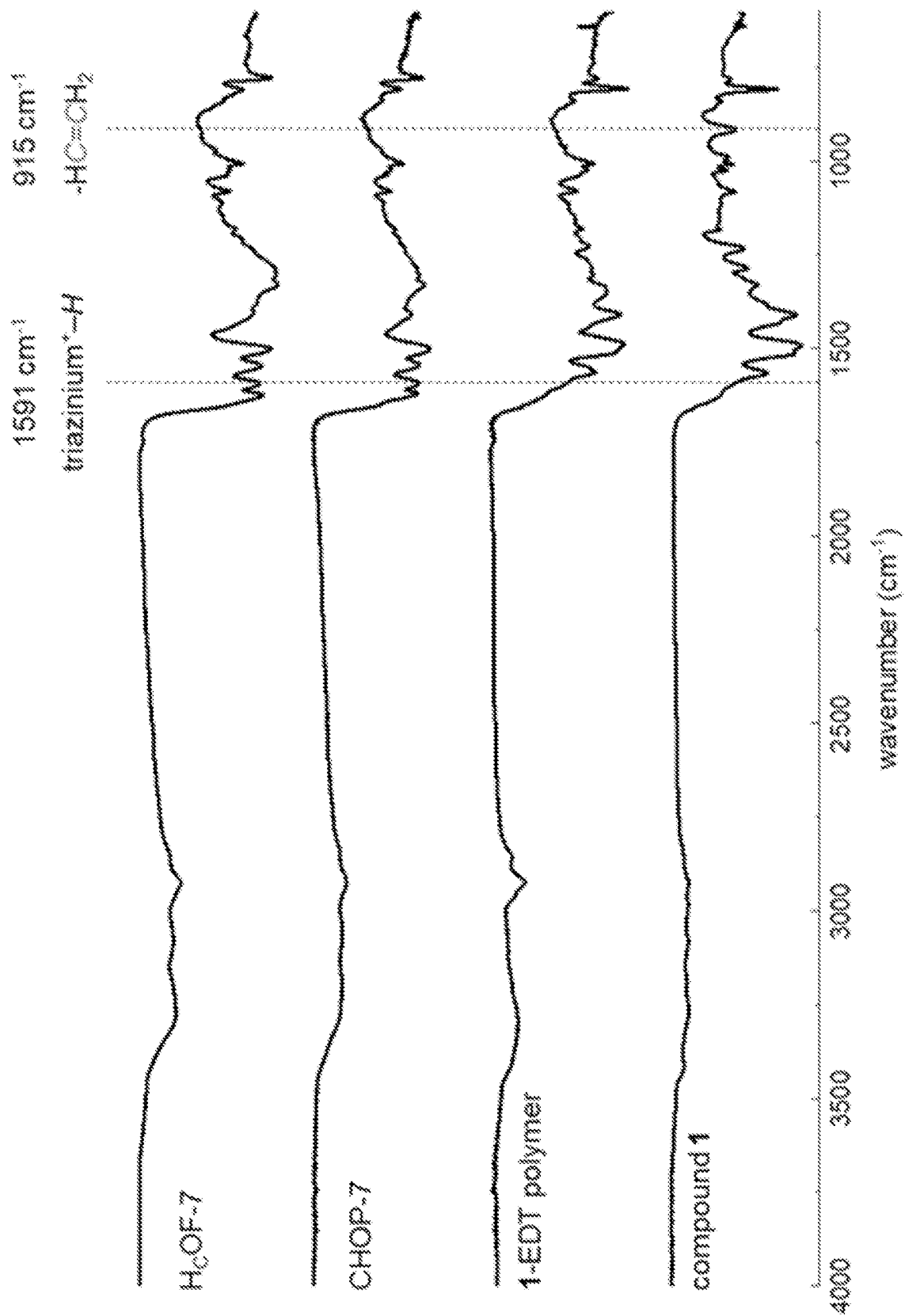


Figure 22

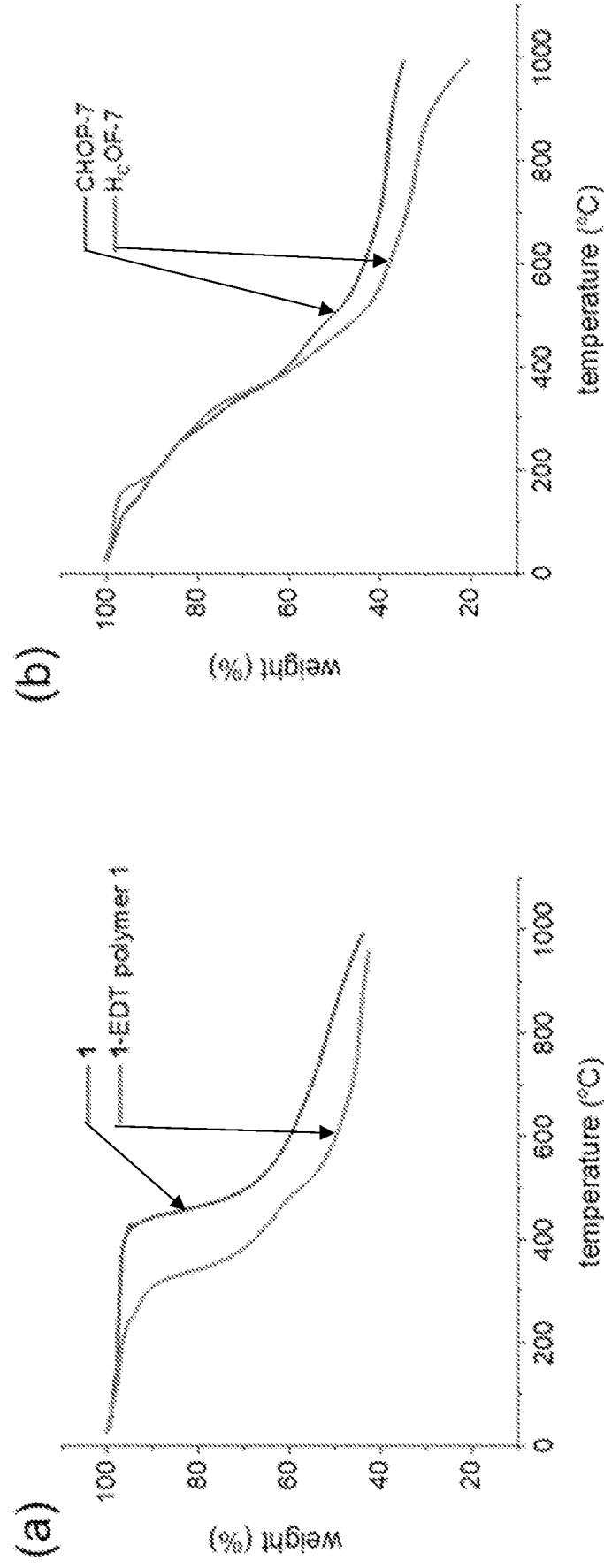


Figure 23

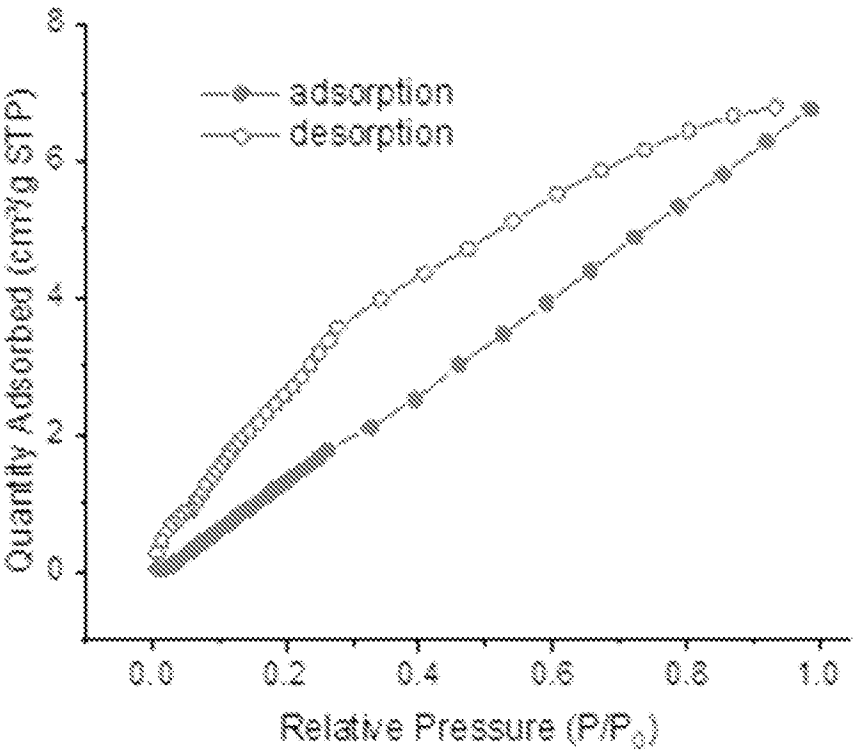


Figure 24

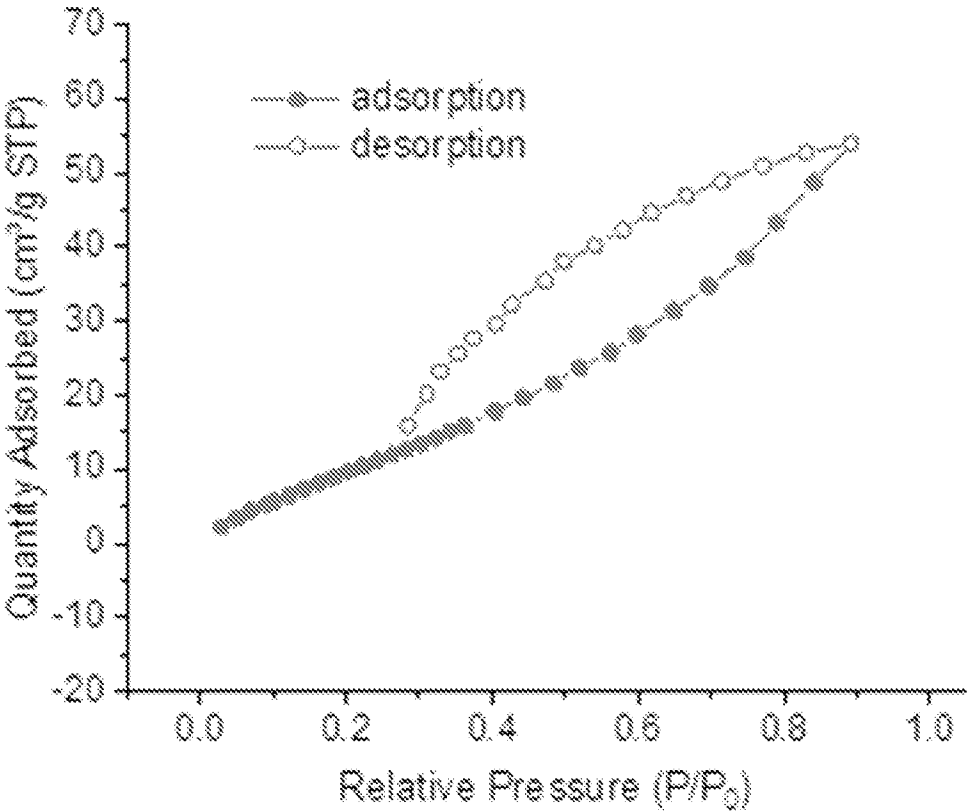


Figure 25

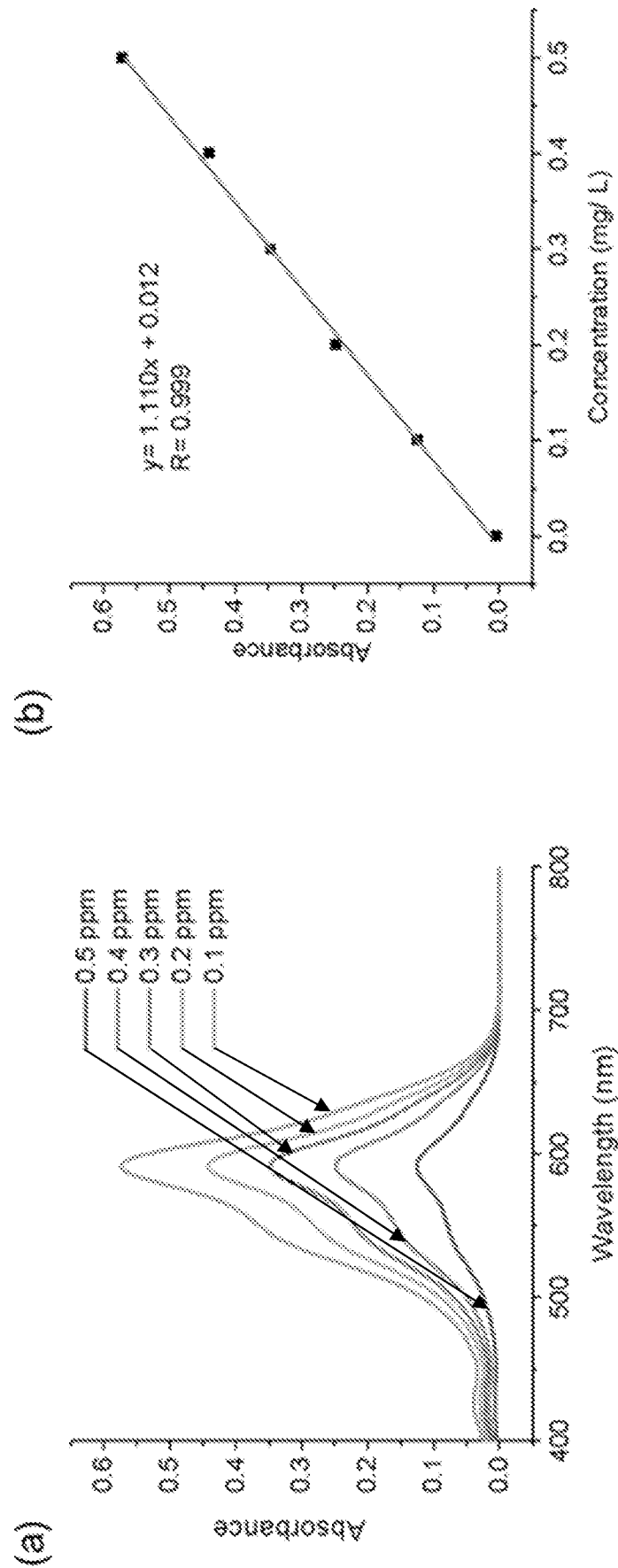


Figure 26

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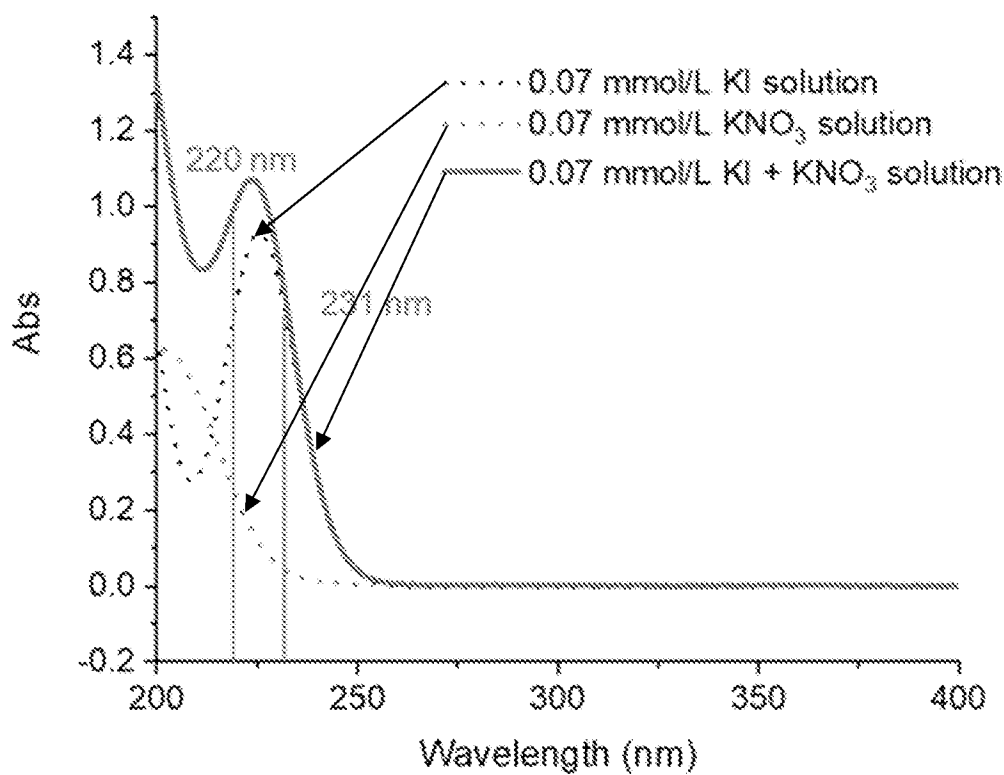


Figure 27

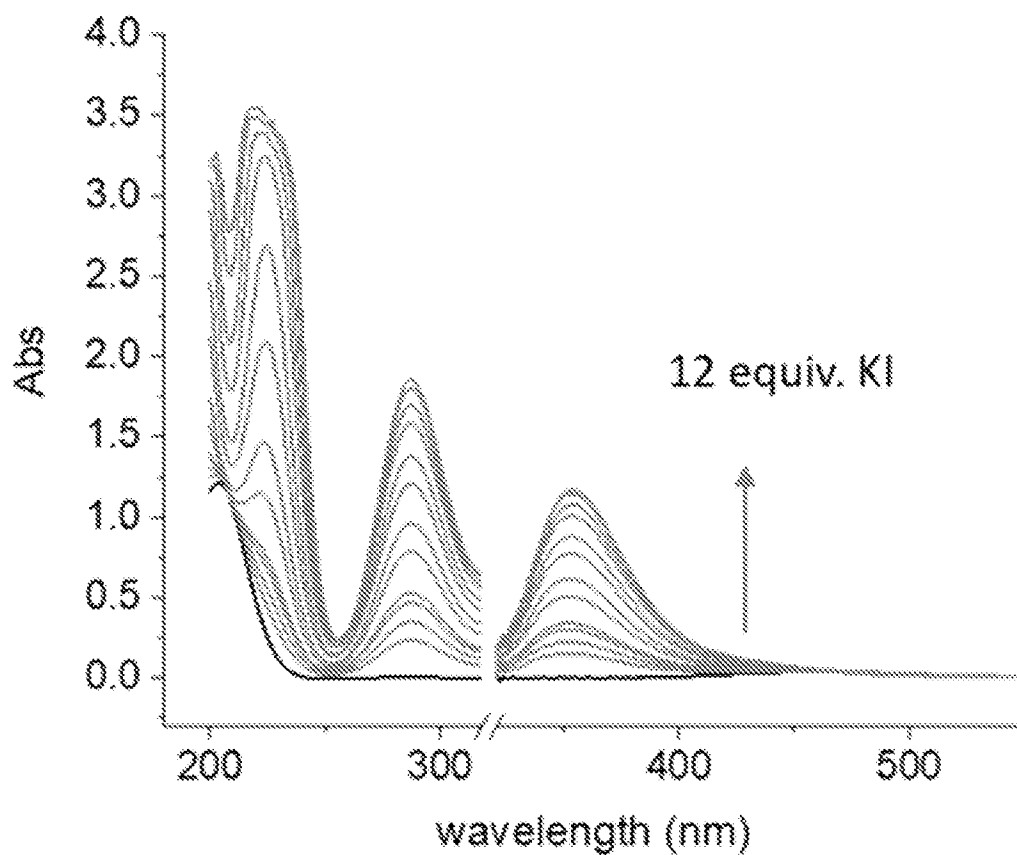


Figure 28

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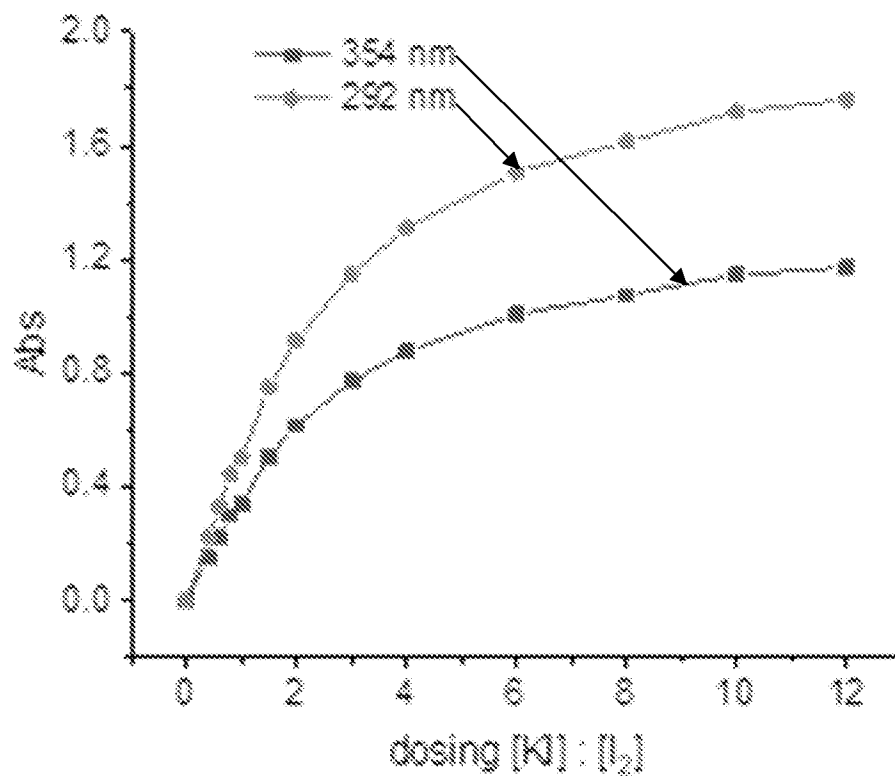


Figure 29

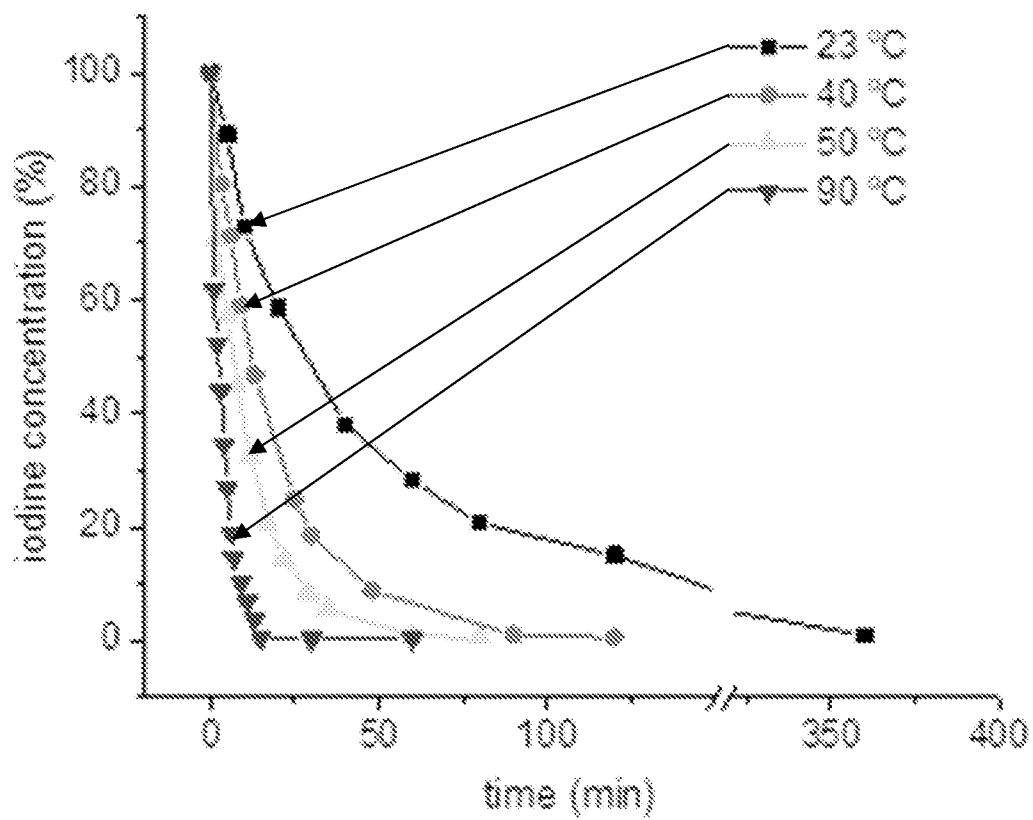


Figure 30

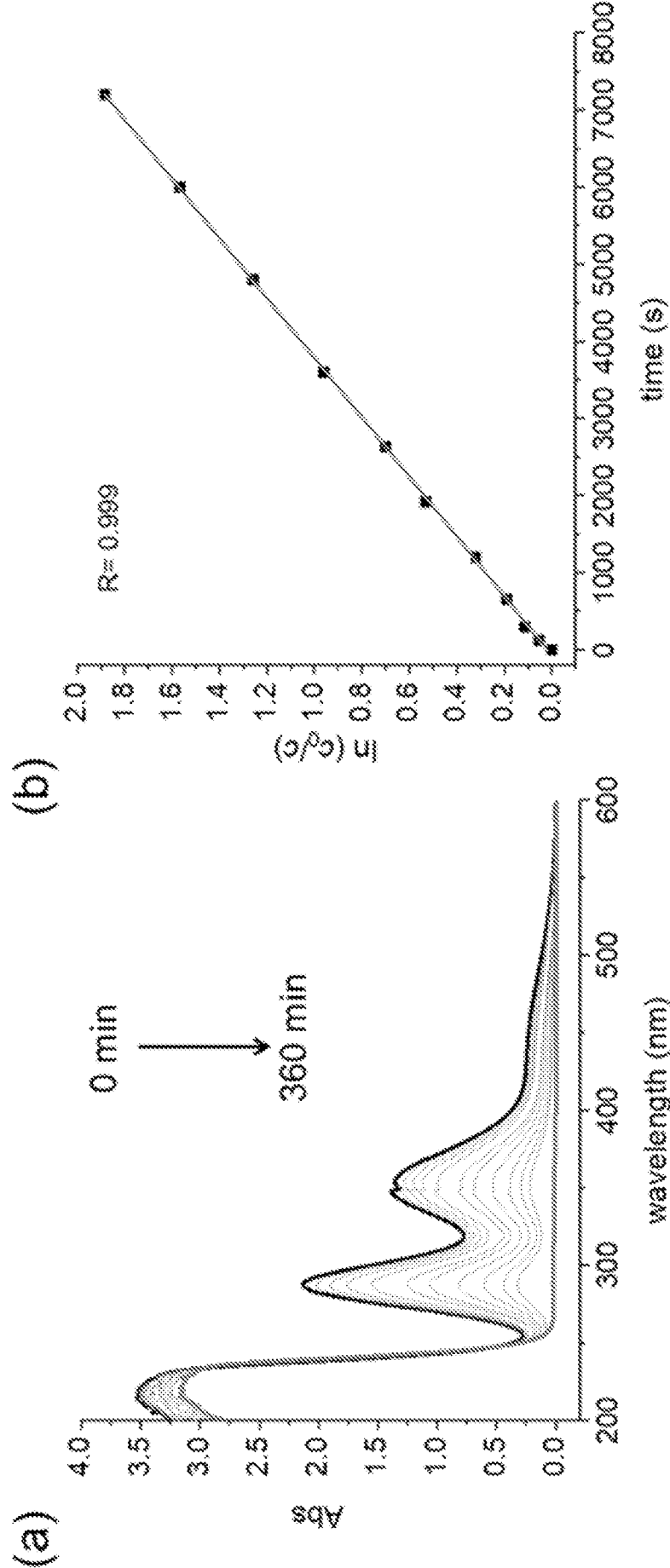


Figure 31

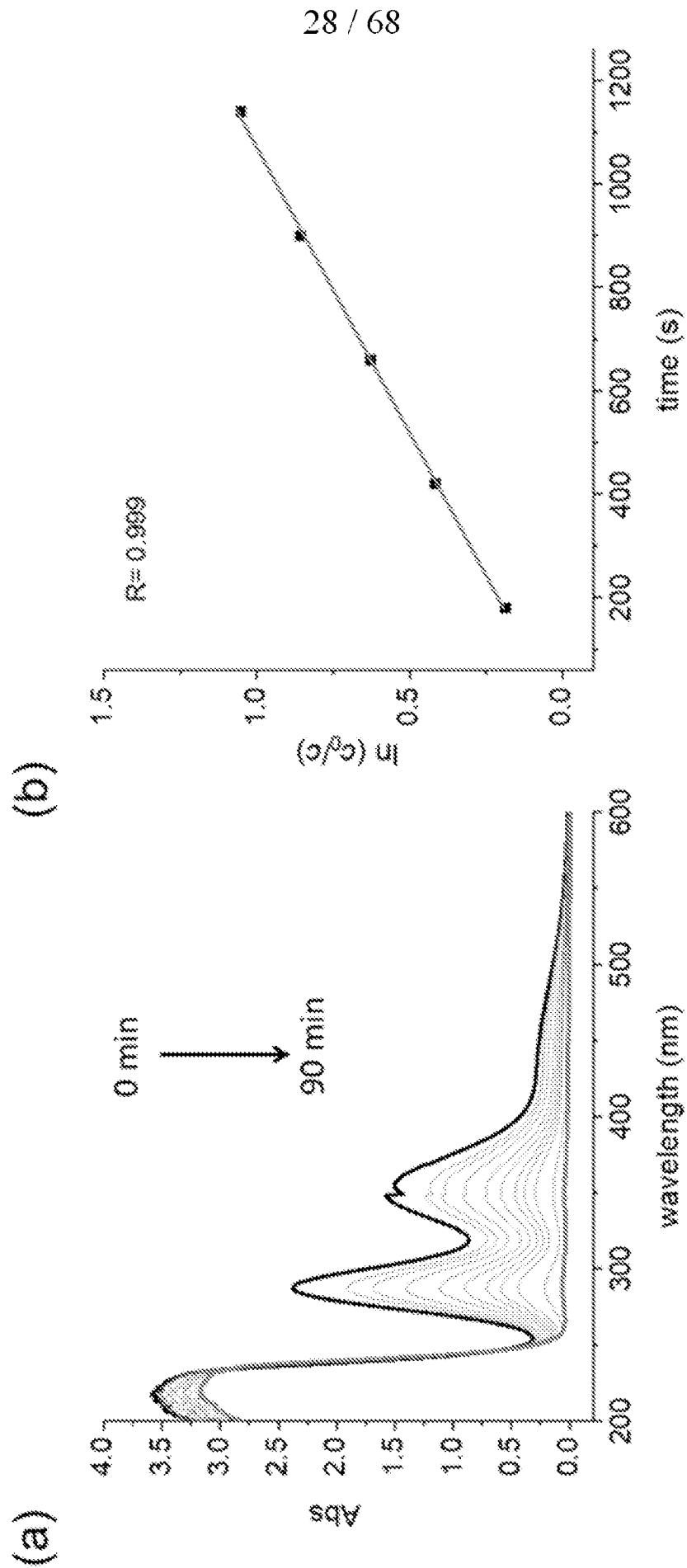


Figure 32

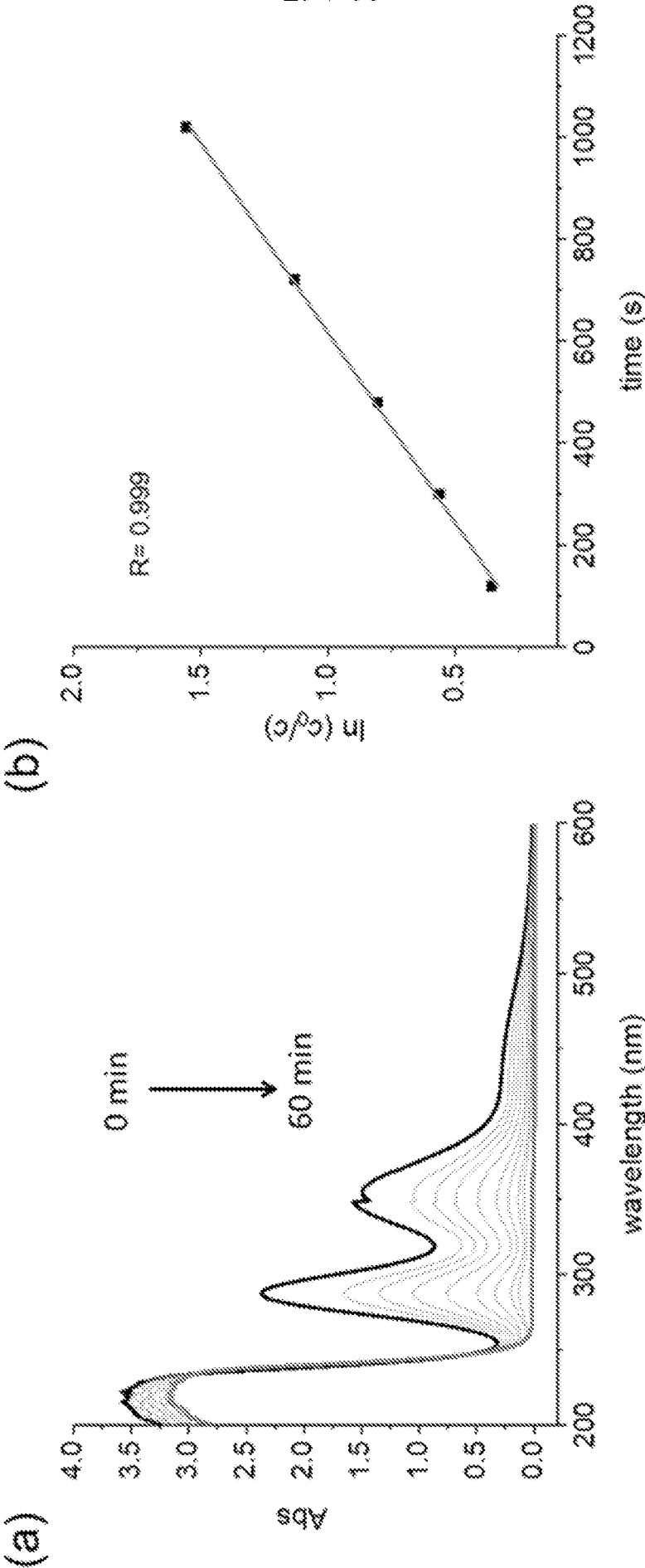


Figure 33

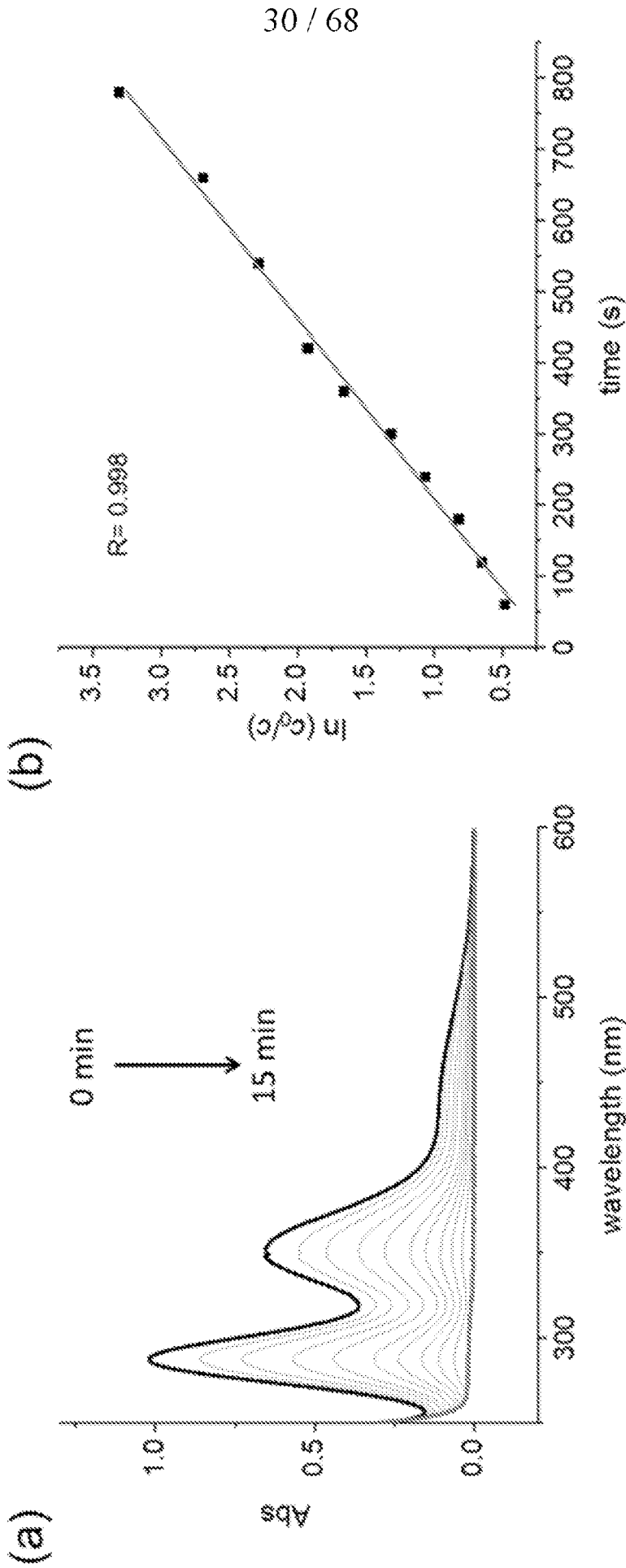


Figure 34

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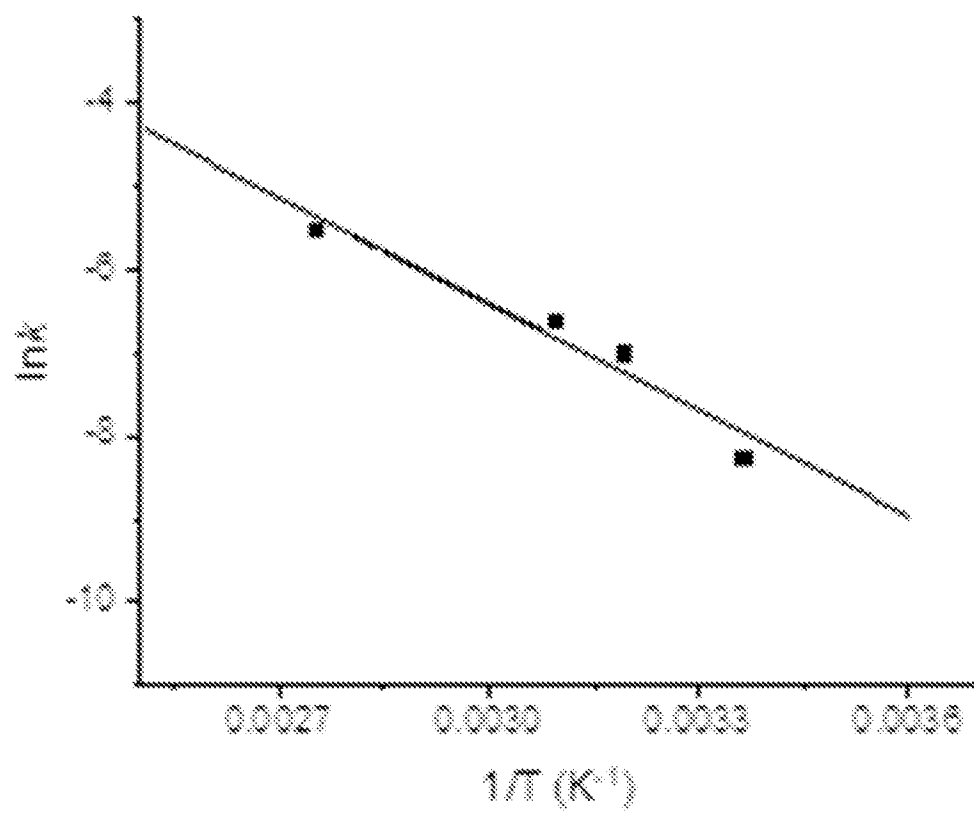


Figure 35

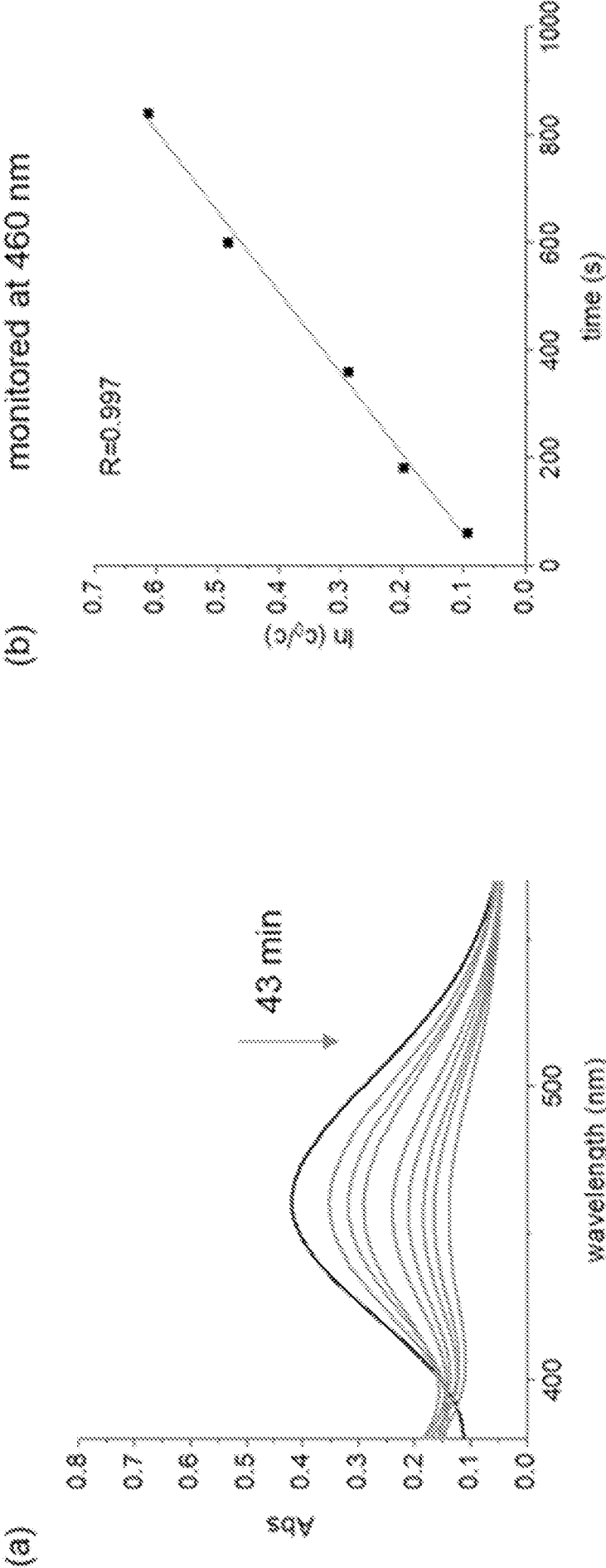
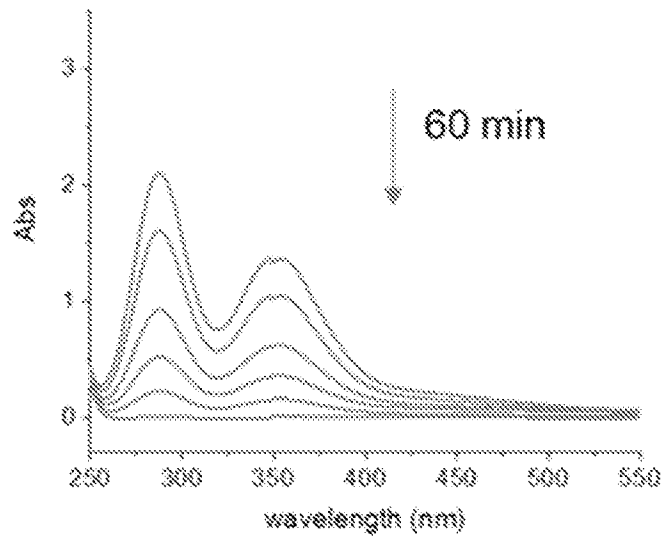
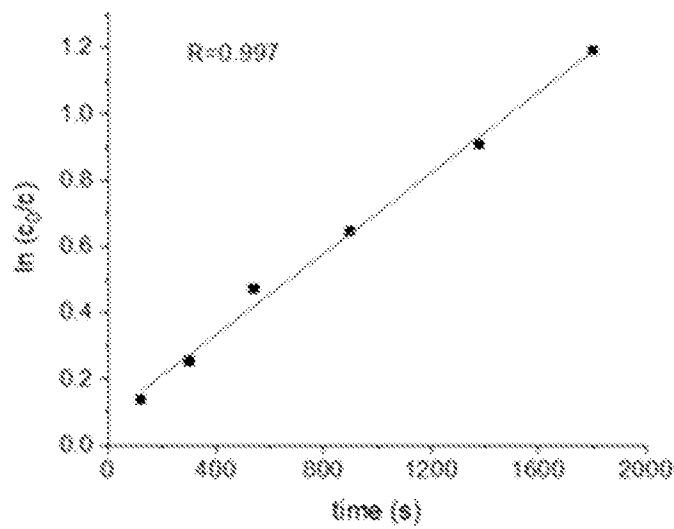


Figure 36

(a) 33 / 68



(b) monitored at 460 nm



(c) monitored at 400 nm

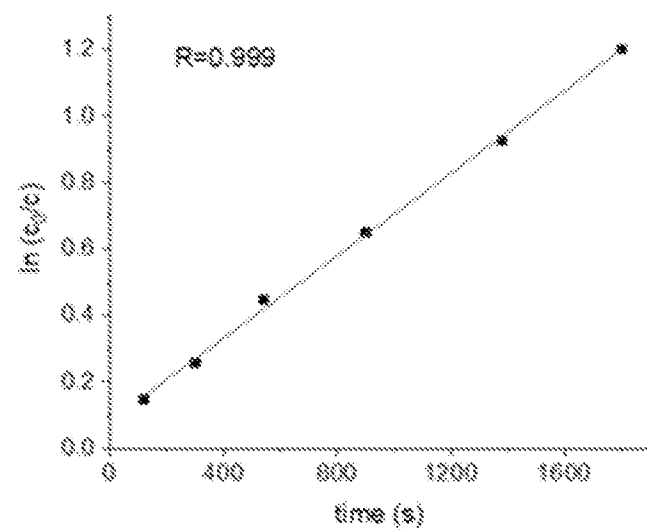
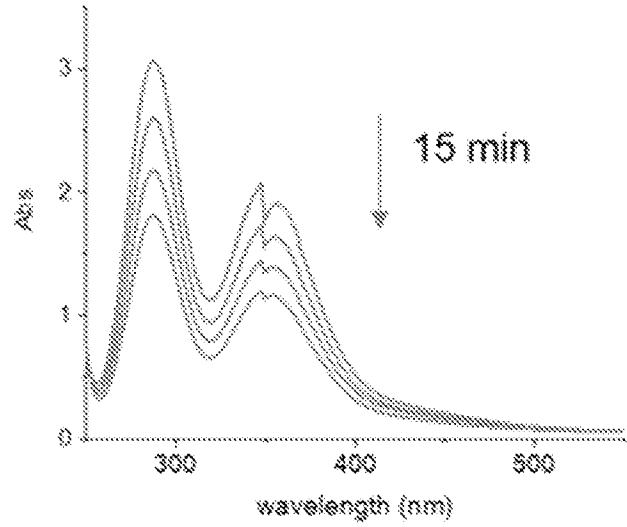
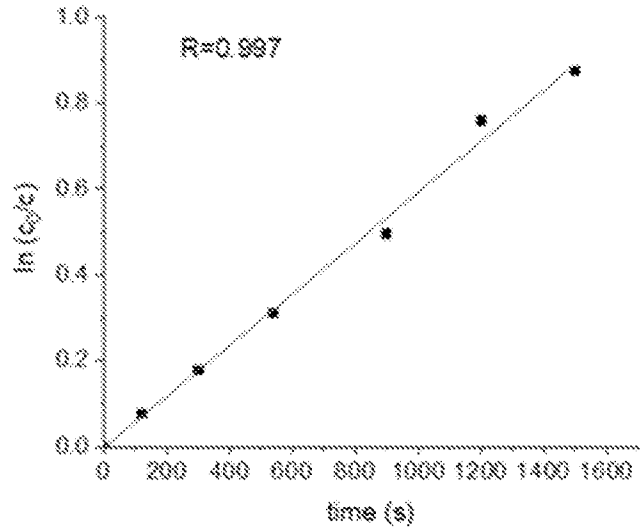


Figure 37

(a) 34 / 68



(b) monitored at 460 nm



(c) monitored at 400 nm

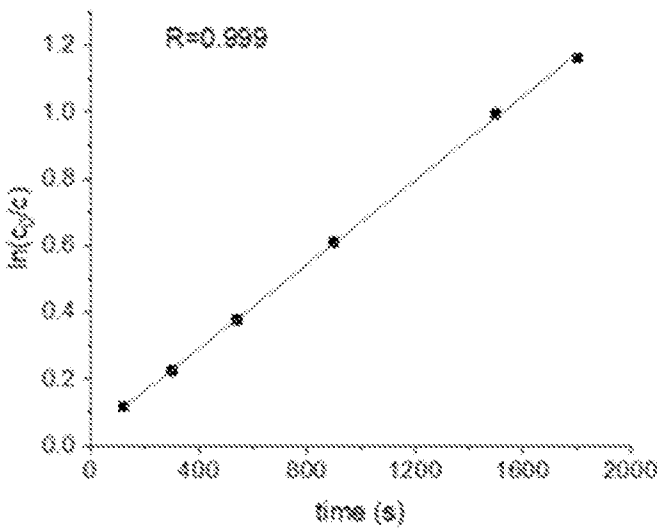
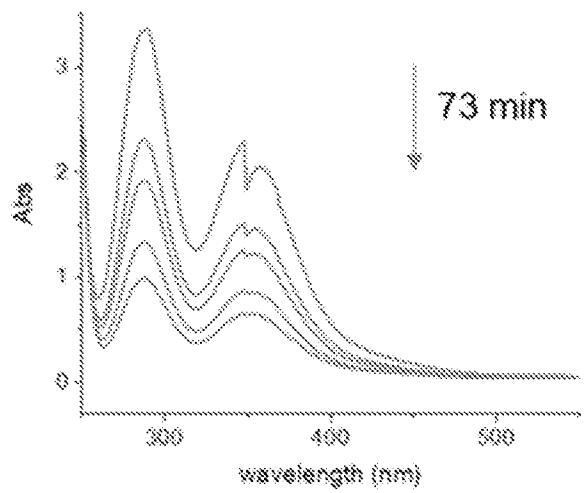
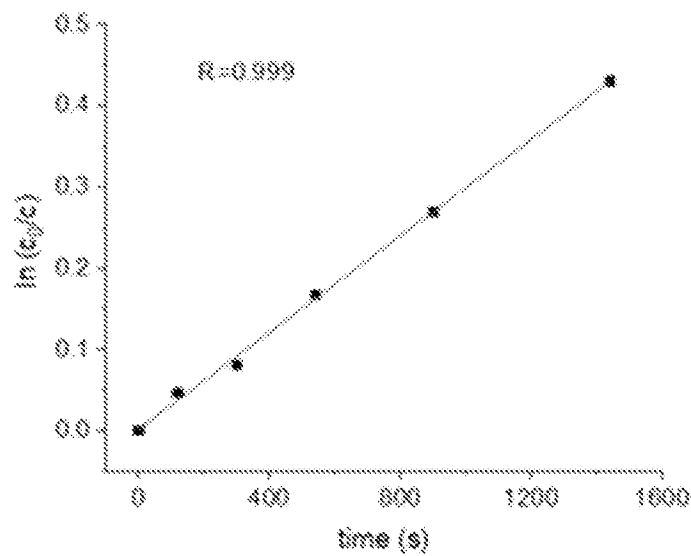


Figure 38

(a) 35 / 68



(b) monitored at 460 nm



(c) monitored at 400 nm

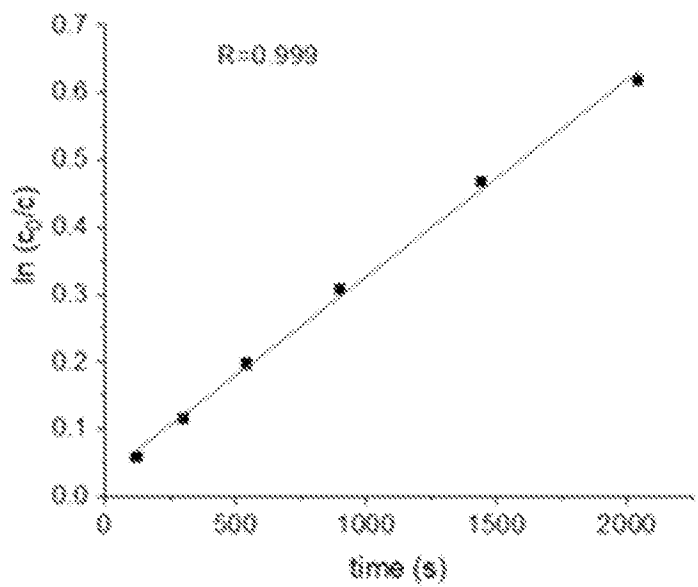


Figure 39

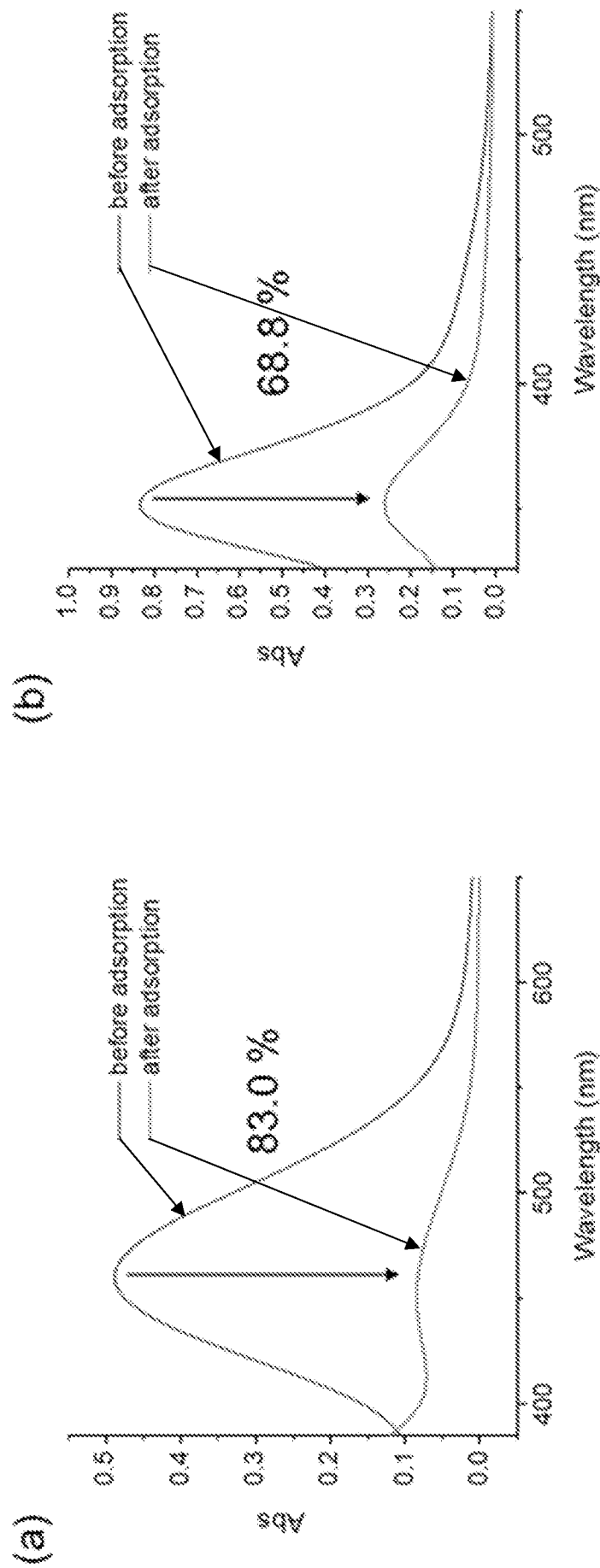


Figure 40

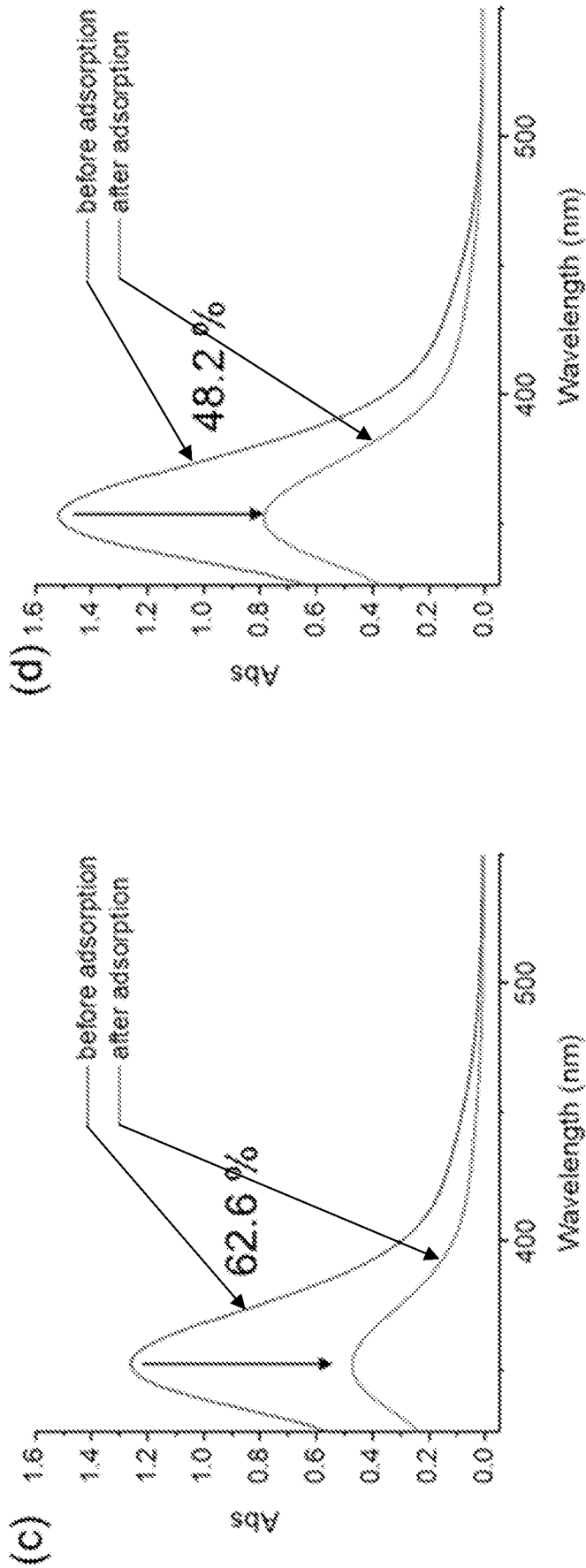


Figure 40 (continued)

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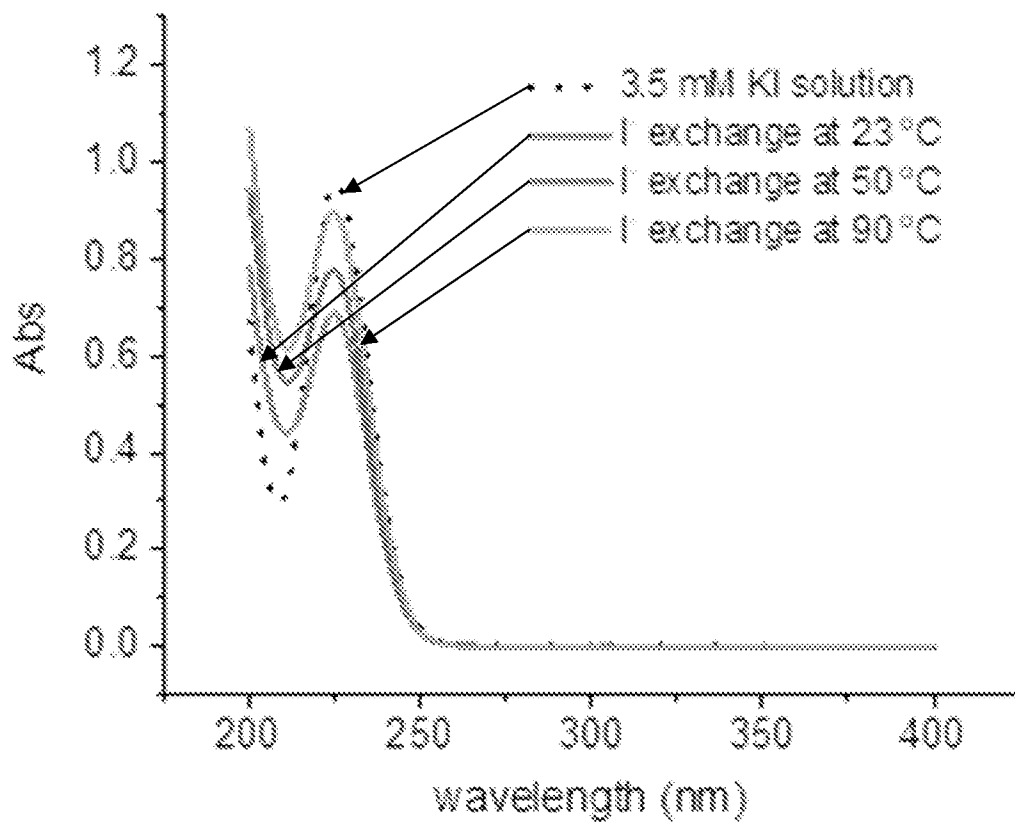


Figure 41

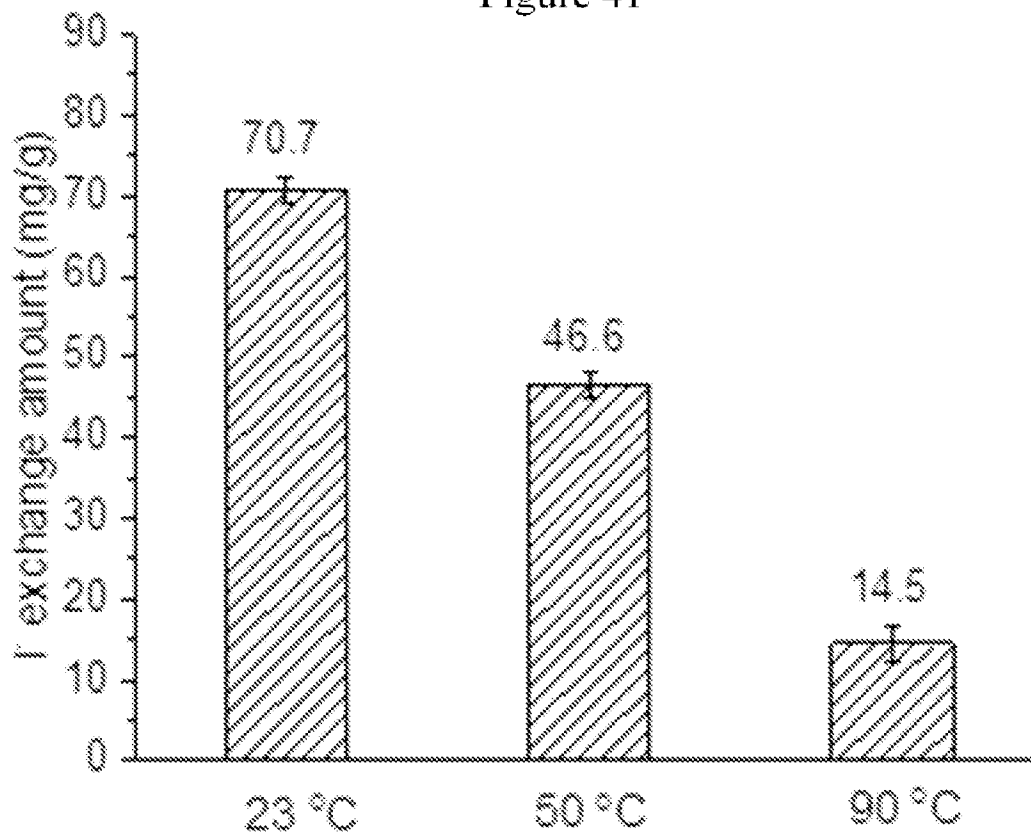


Figure 42

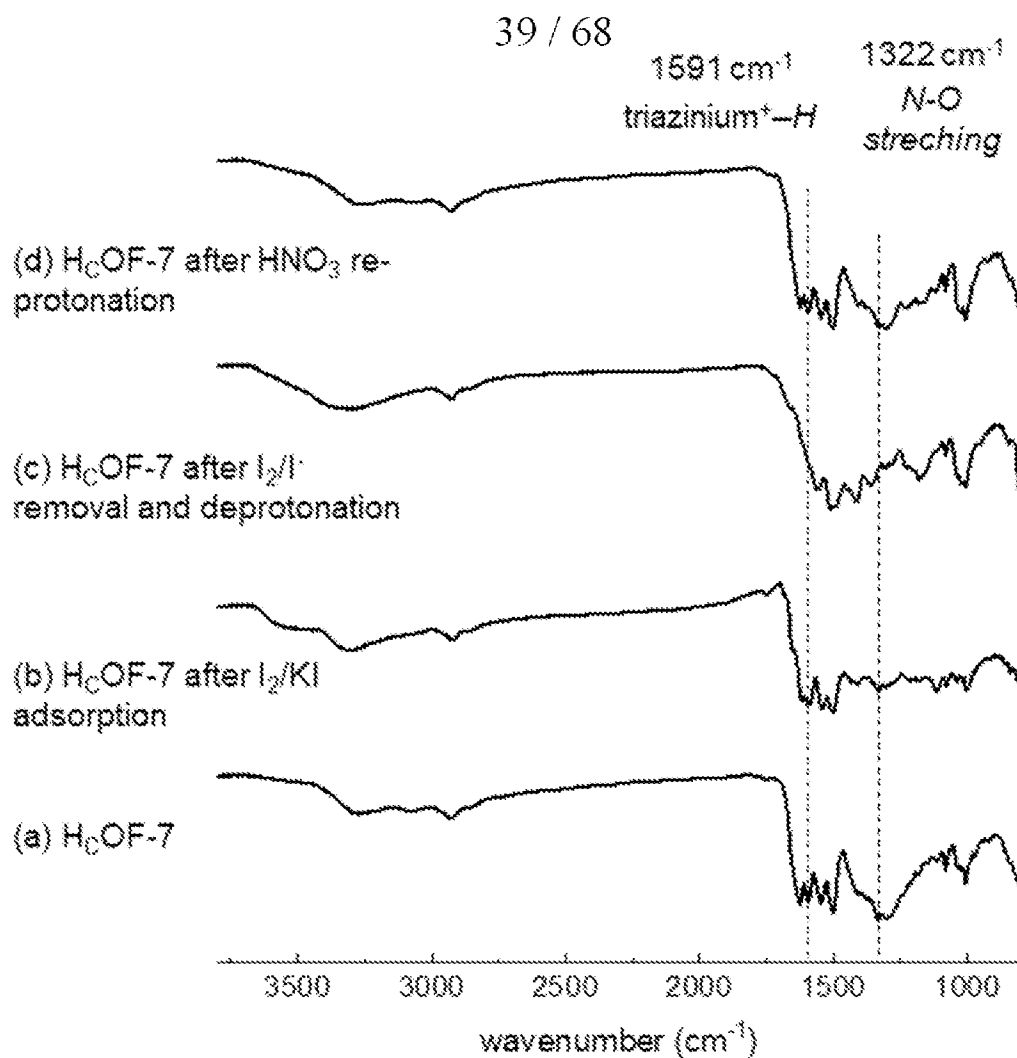


Figure 43

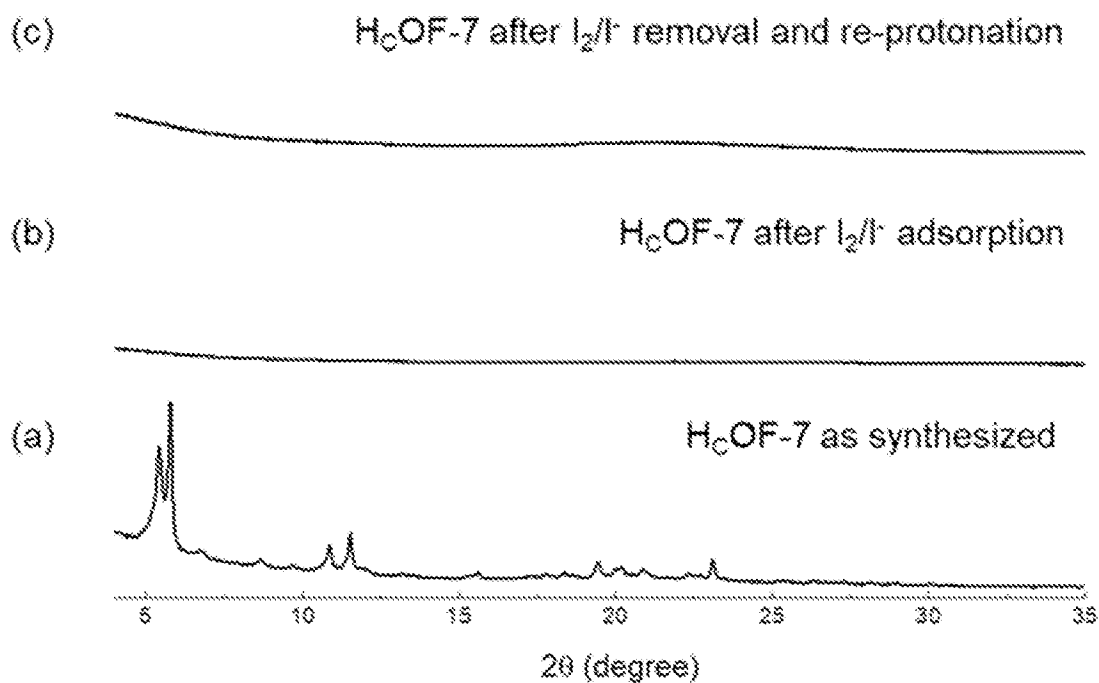


Figure 44

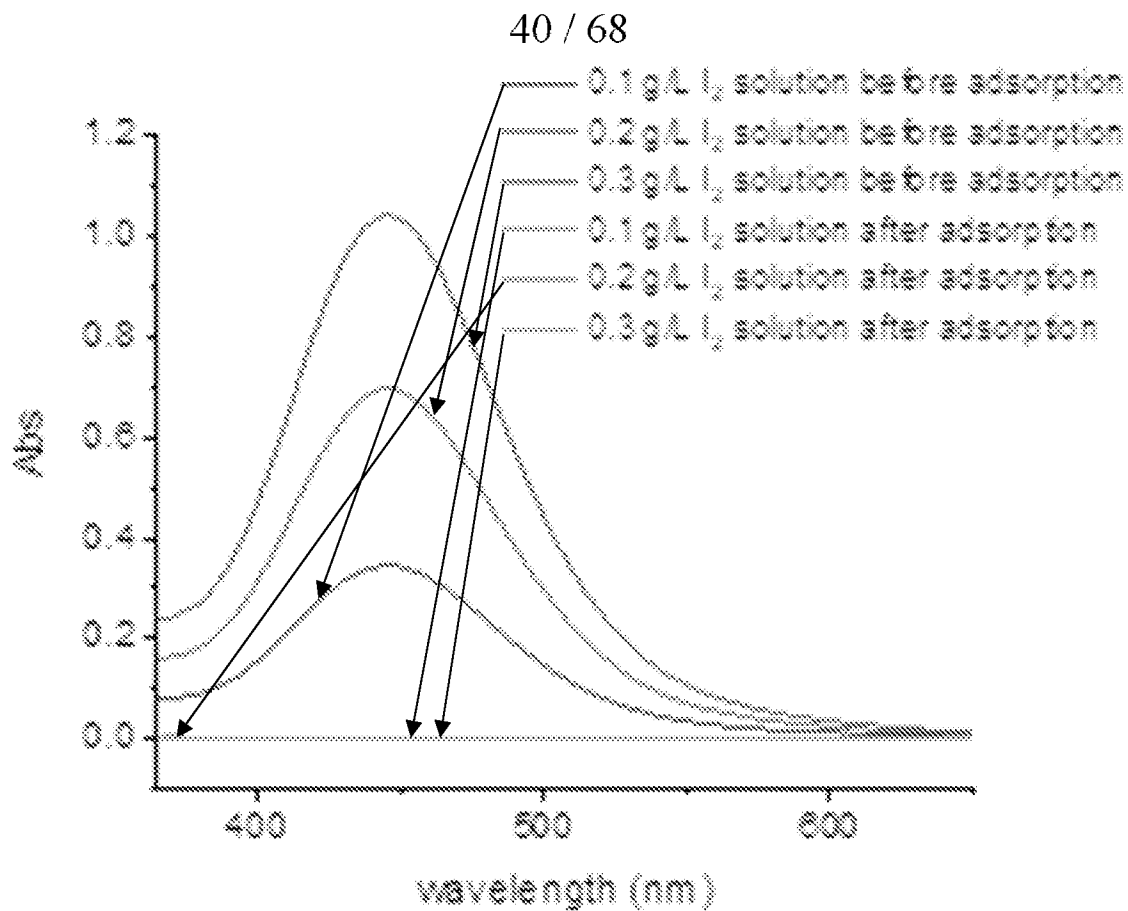


Figure 45

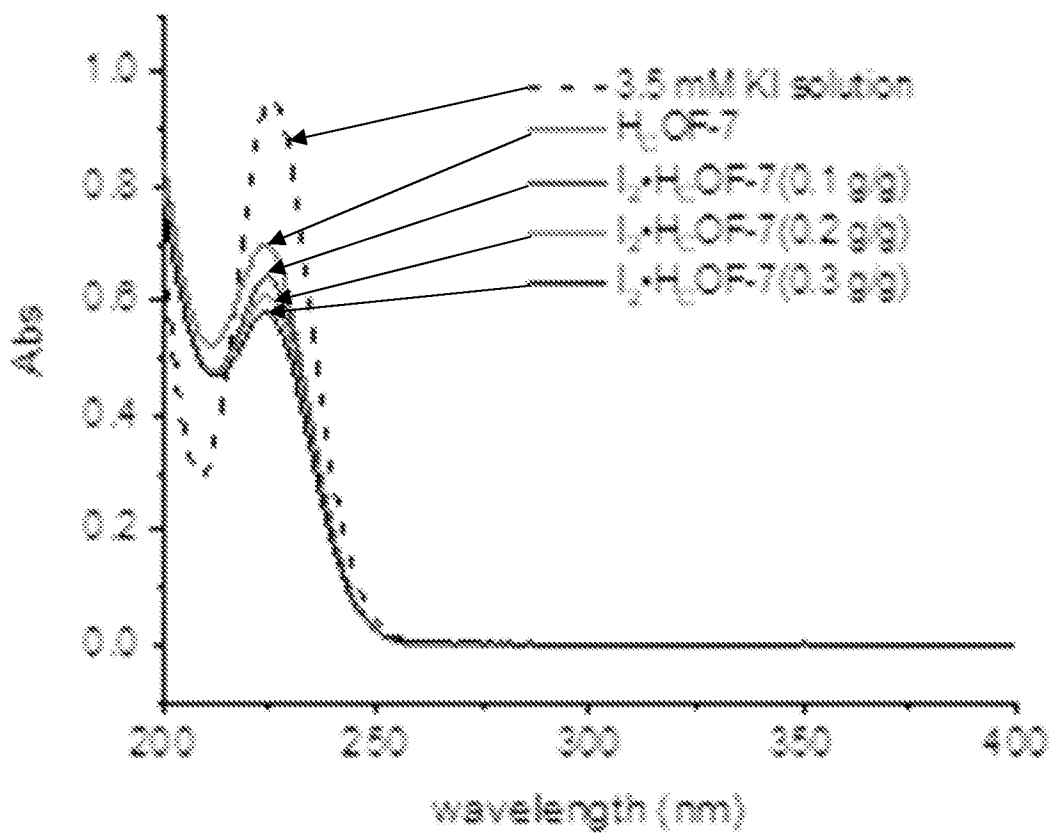


Figure 46

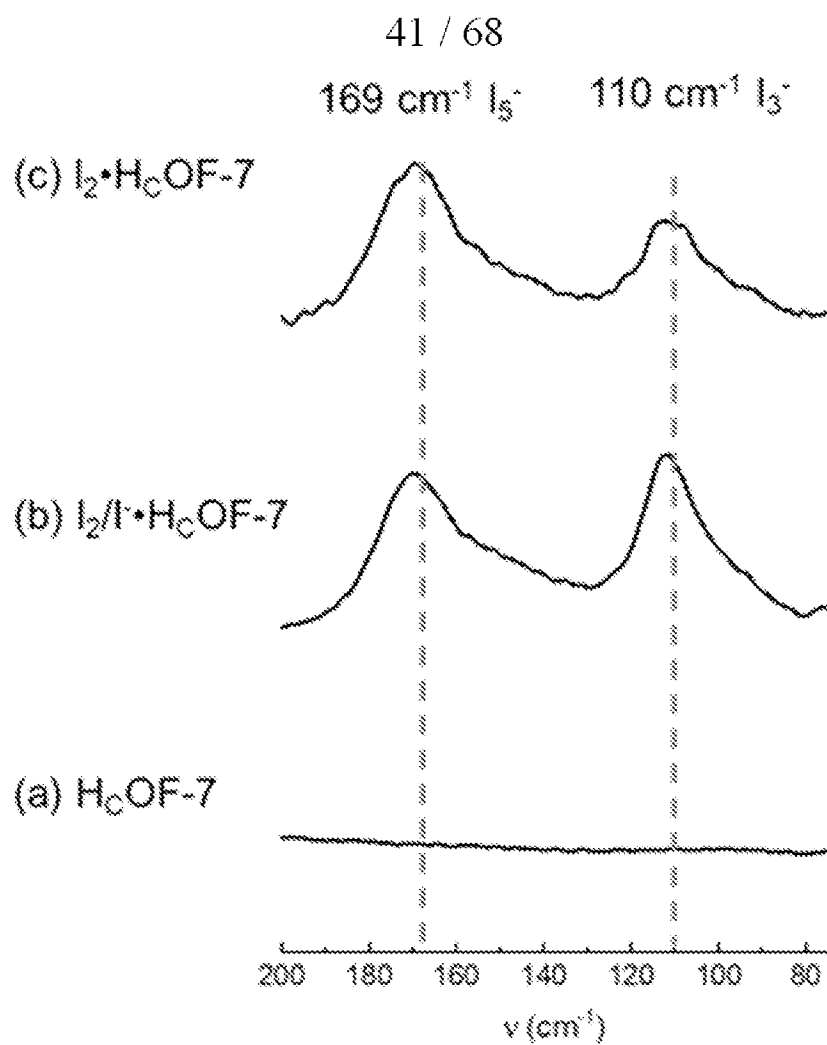


Figure 47

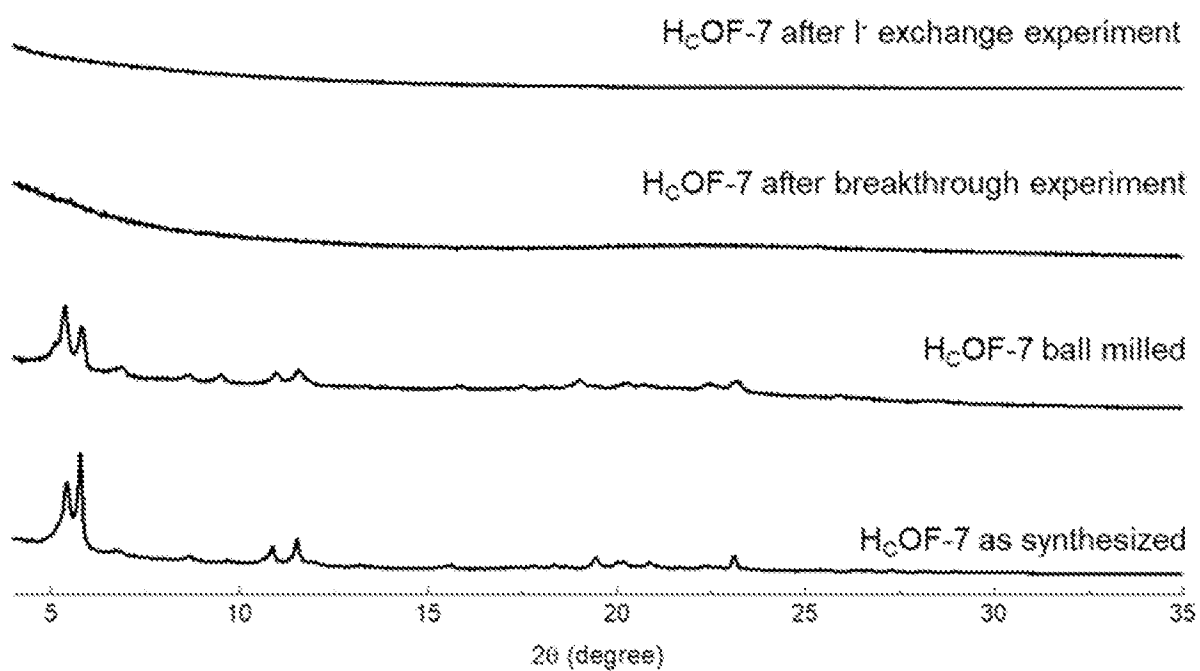


Figure 48

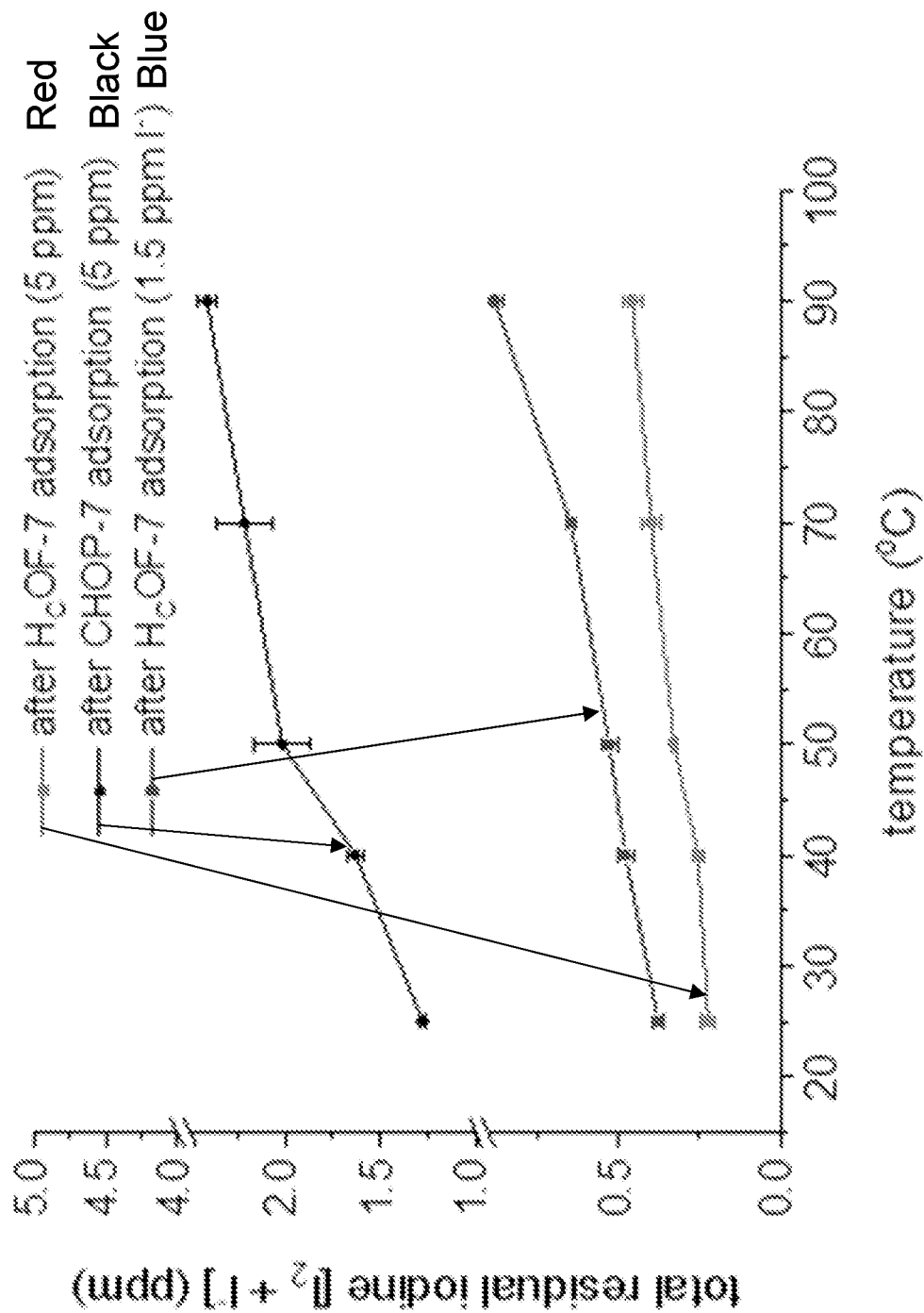


Figure 49

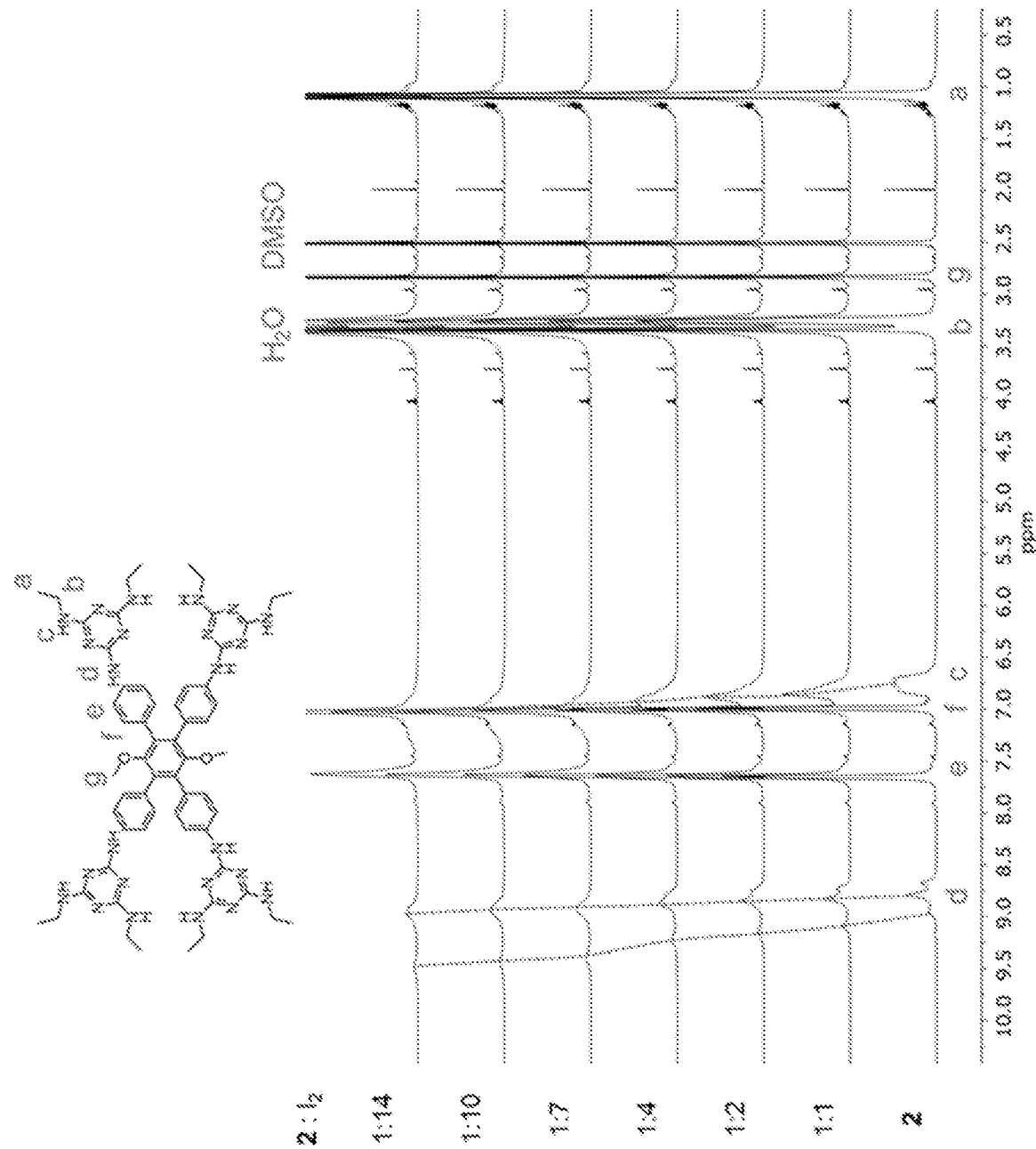


Figure 50

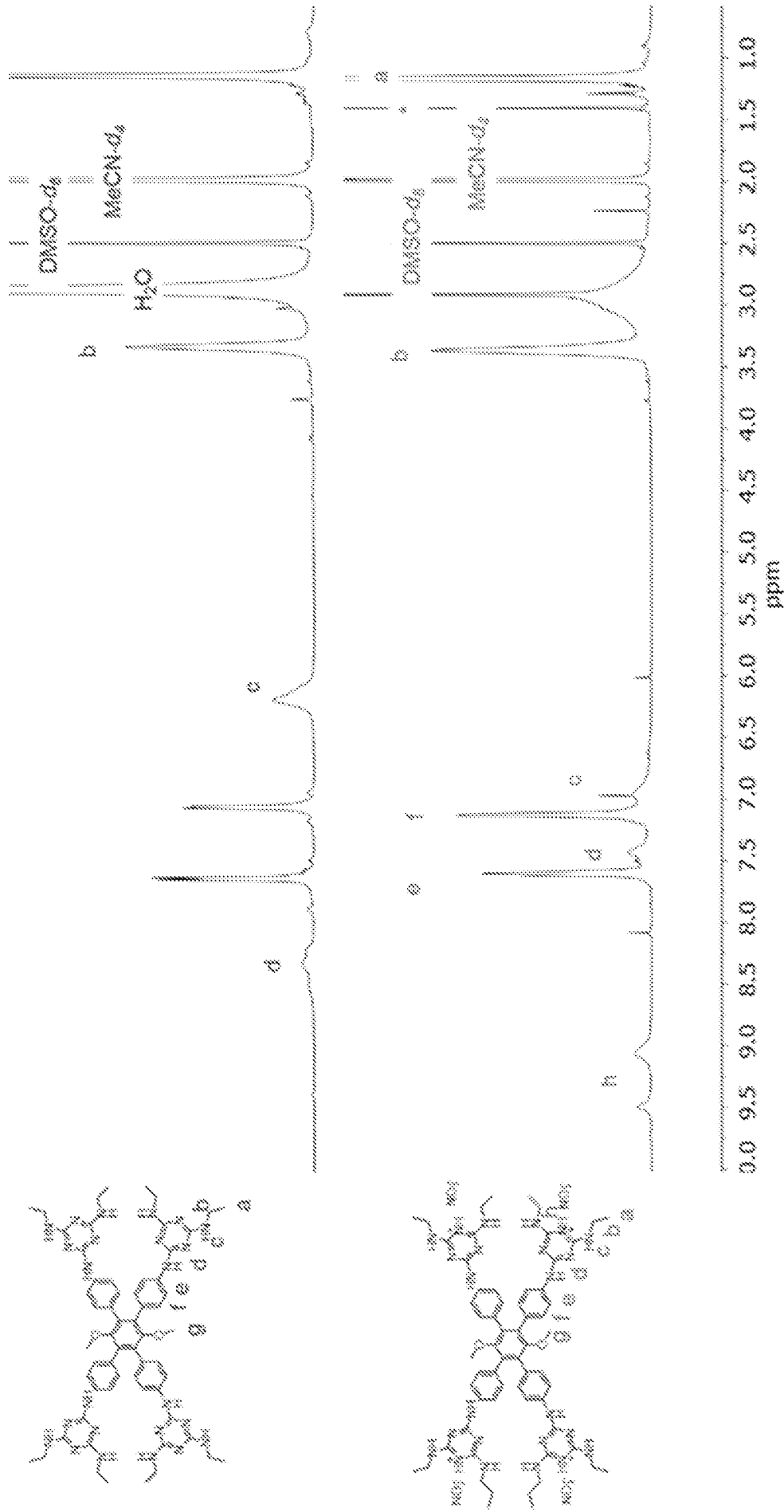


Figure 51

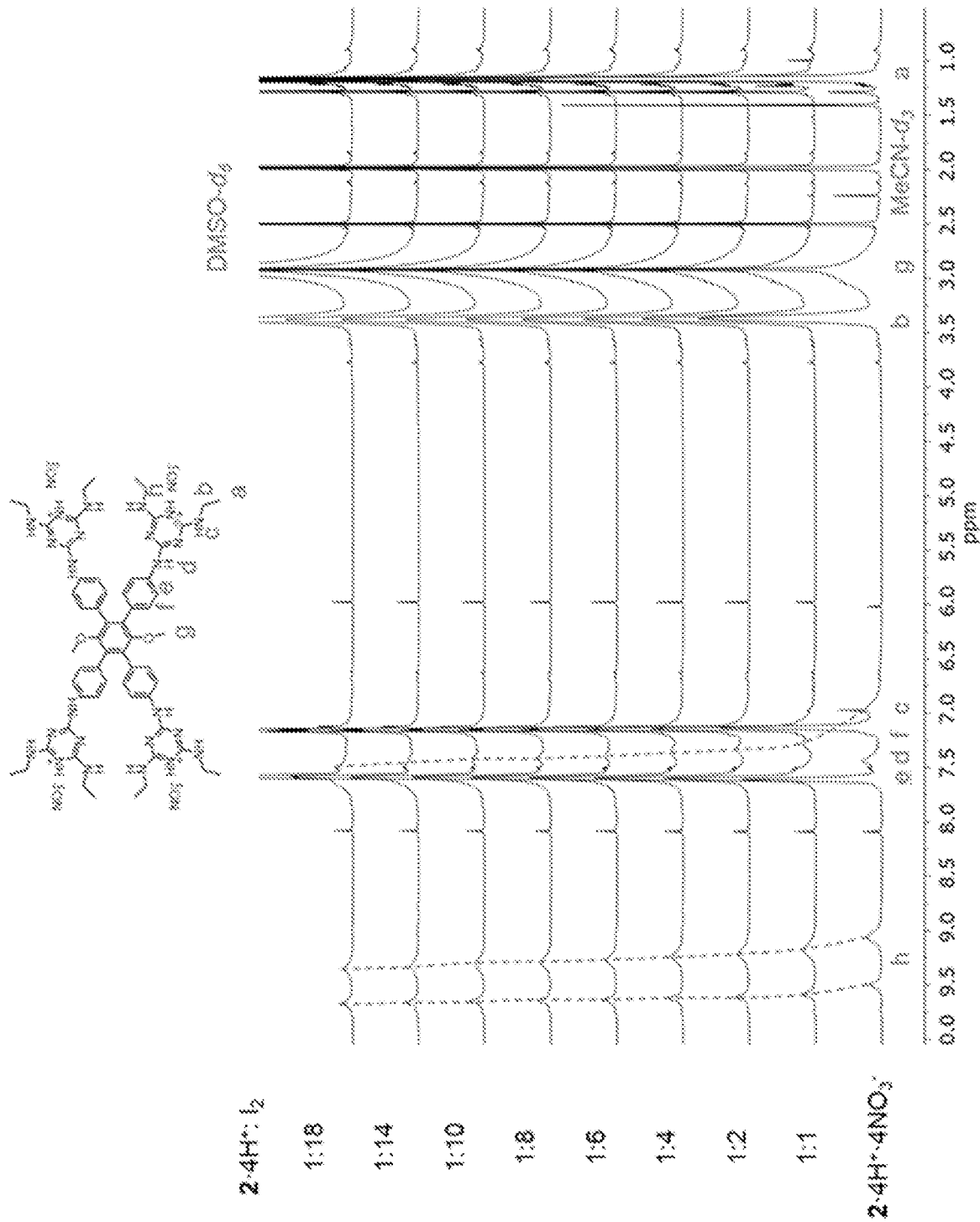


Figure 52

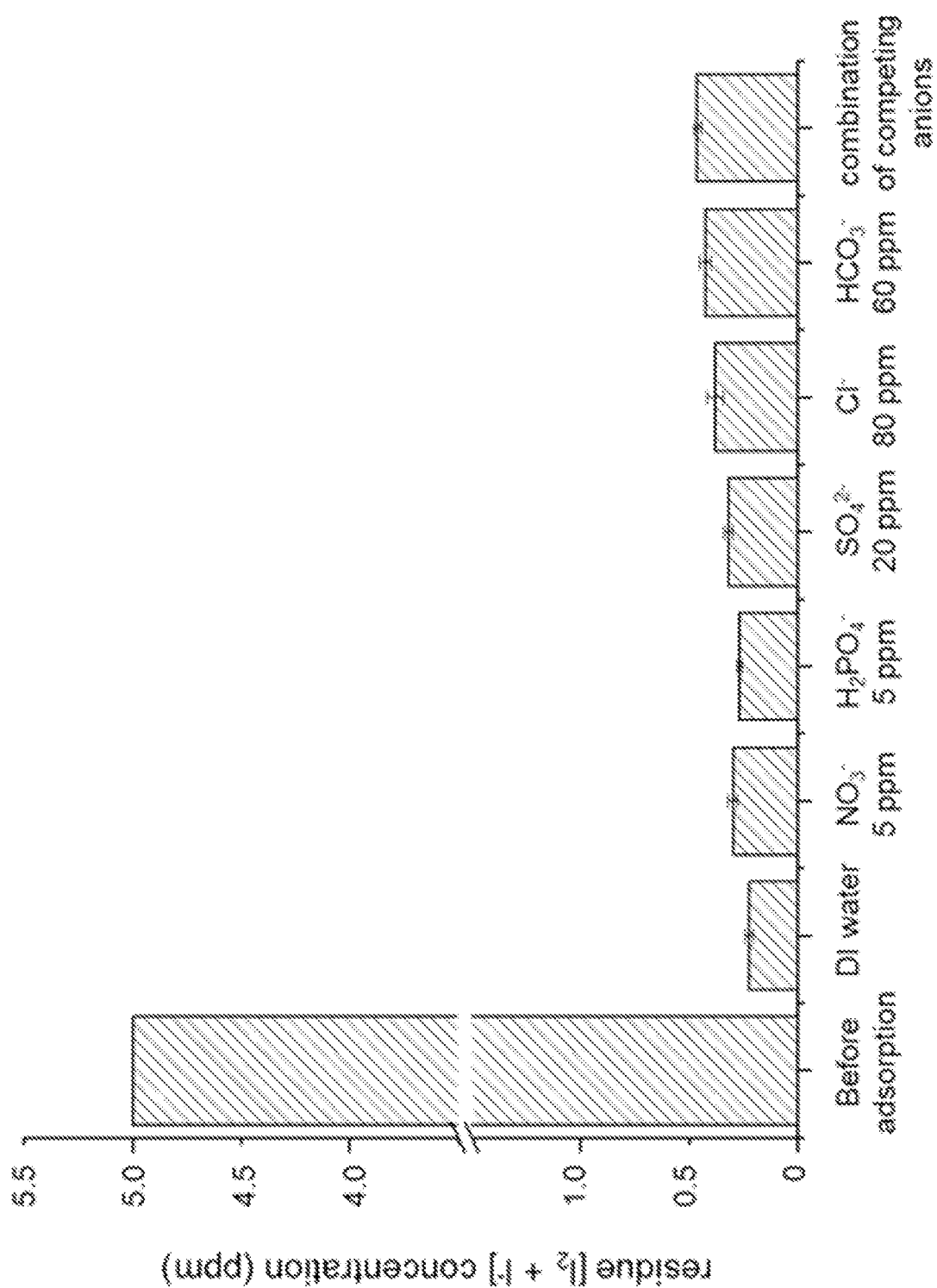


Figure 53

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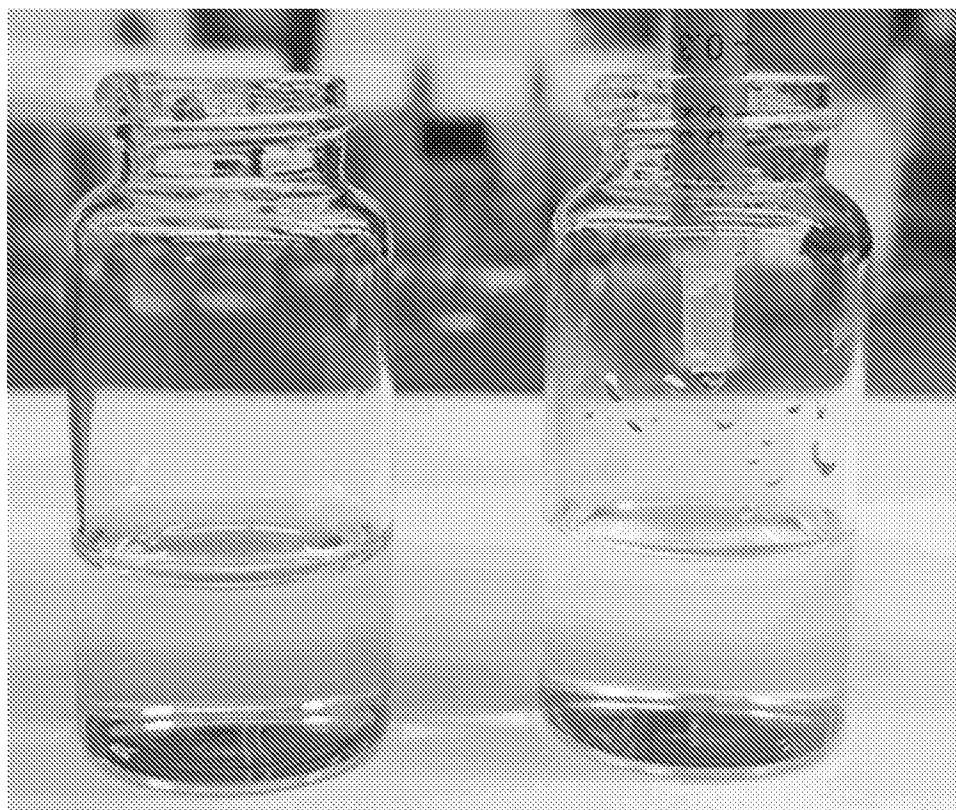


Figure 54

before

after

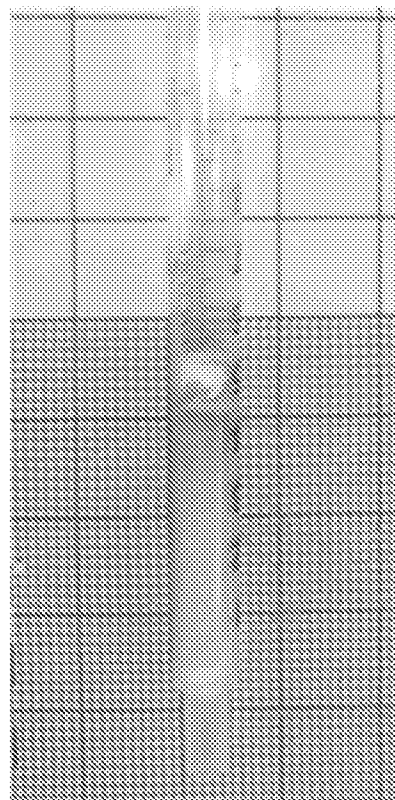
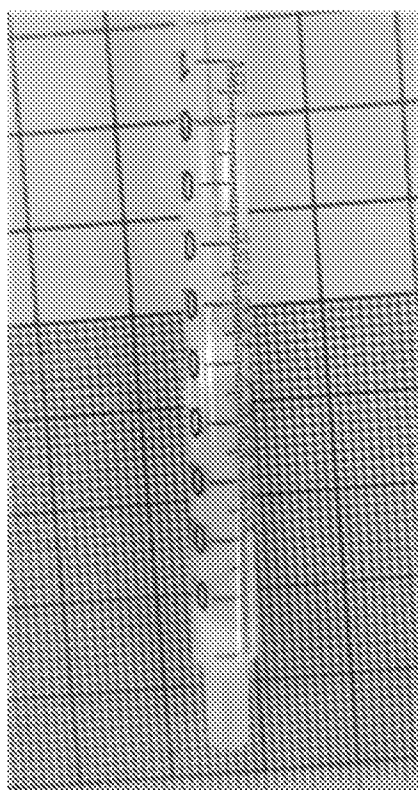


Figure 55

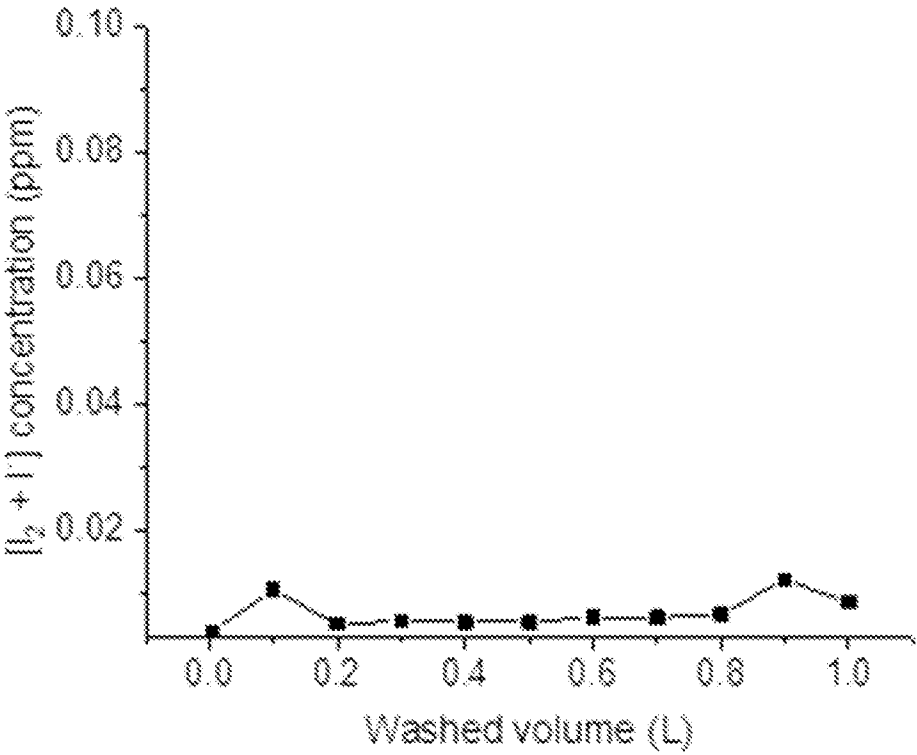


Figure 56

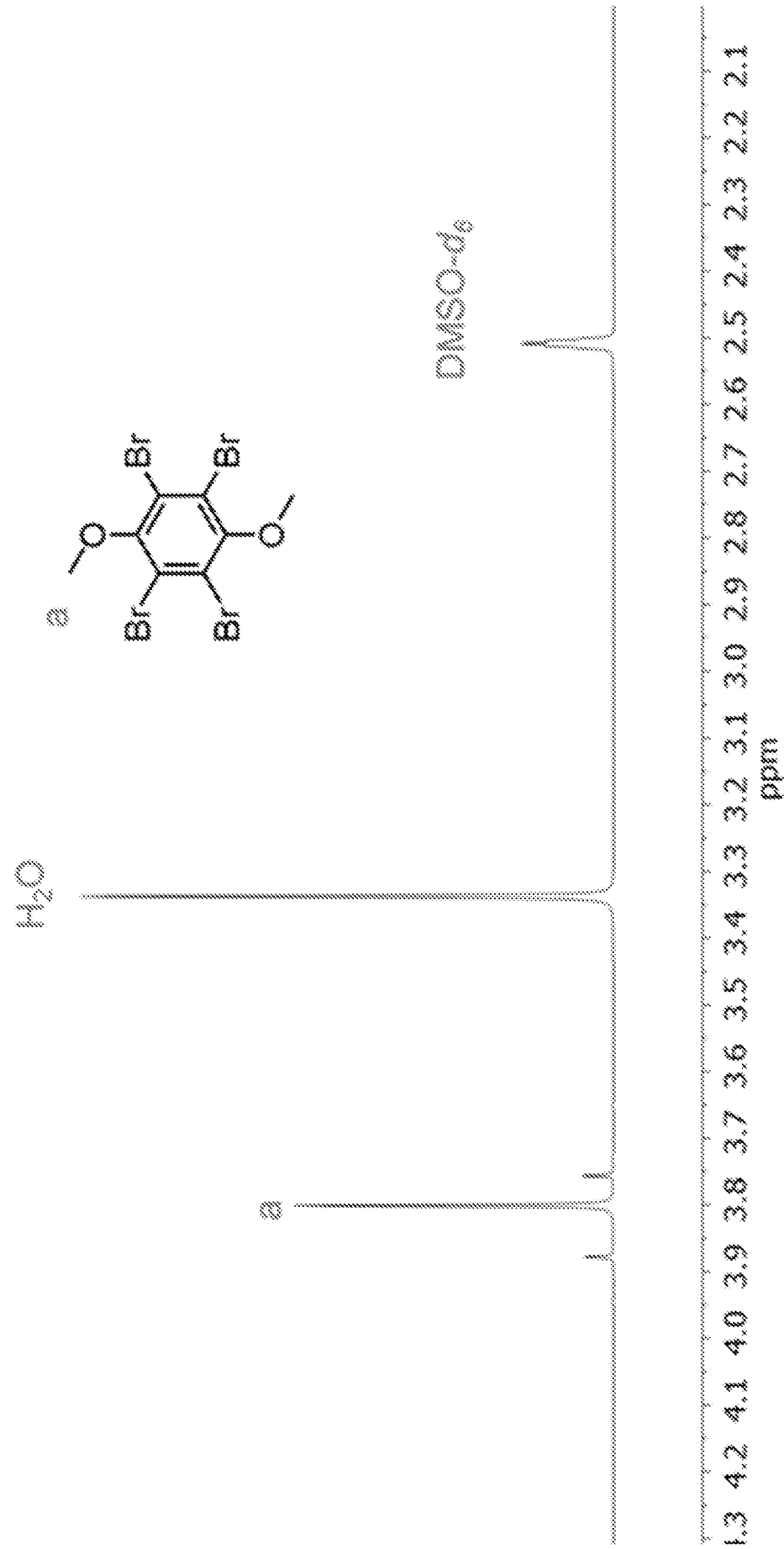


Figure 57

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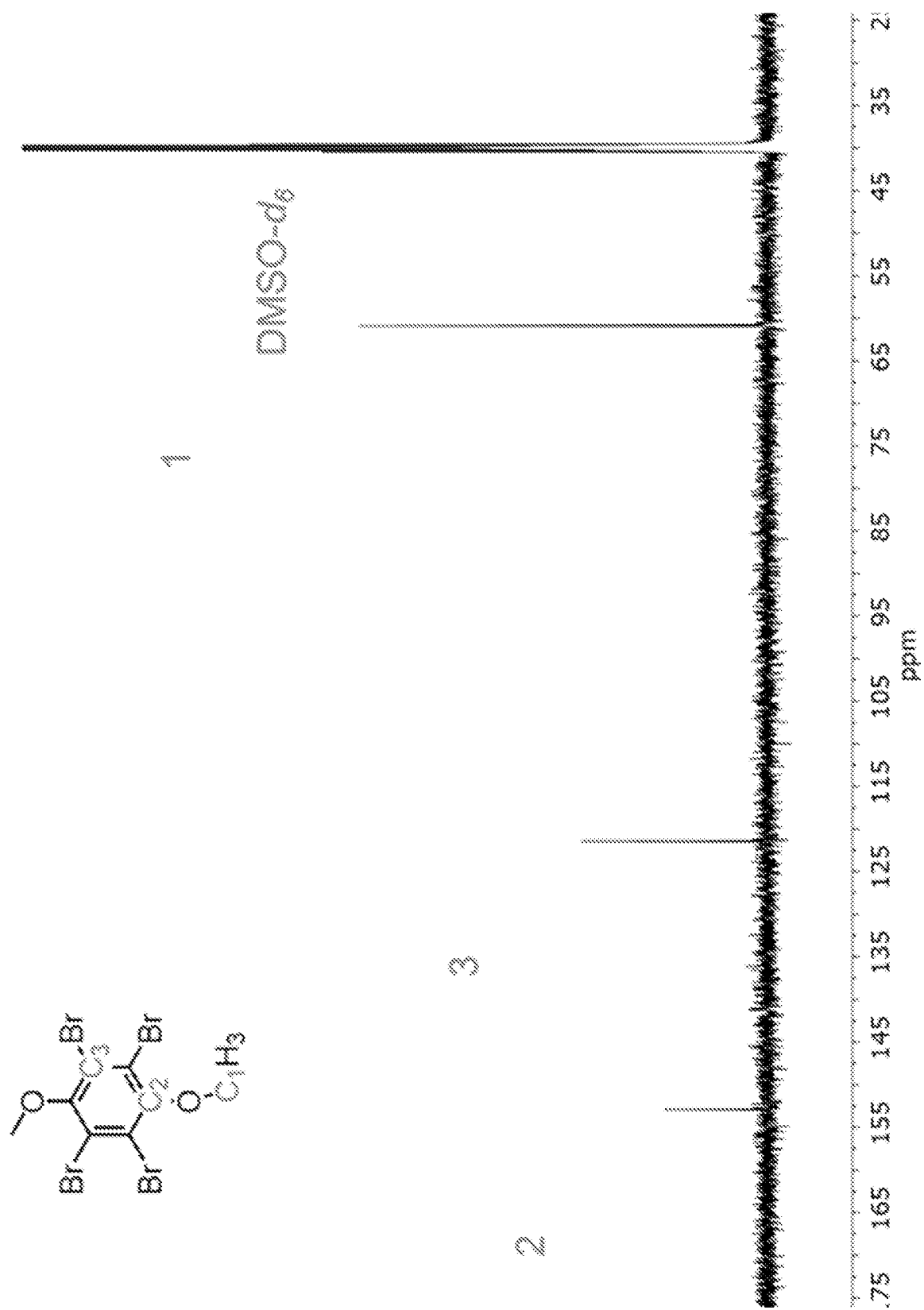


Figure 58

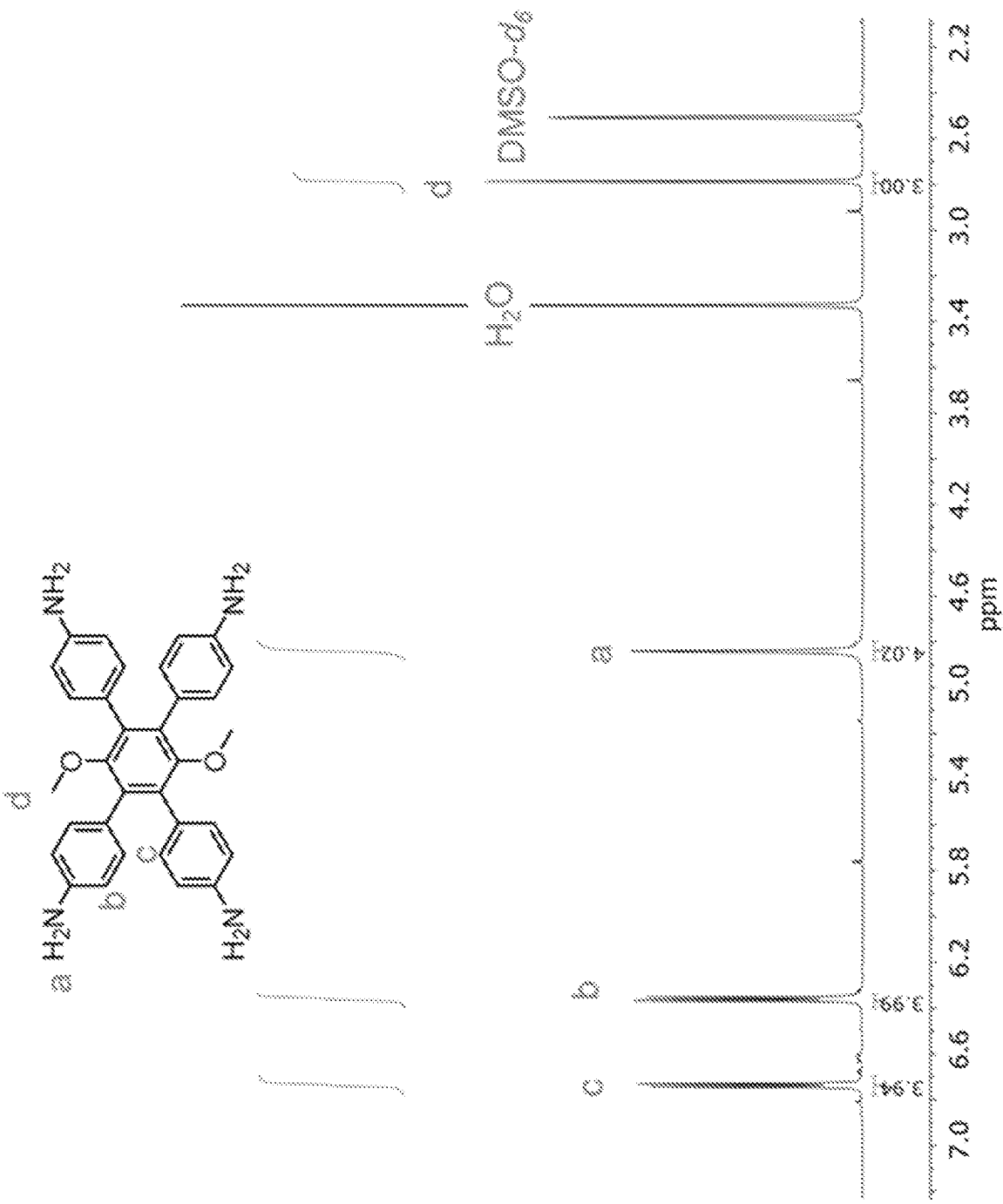


Figure 59

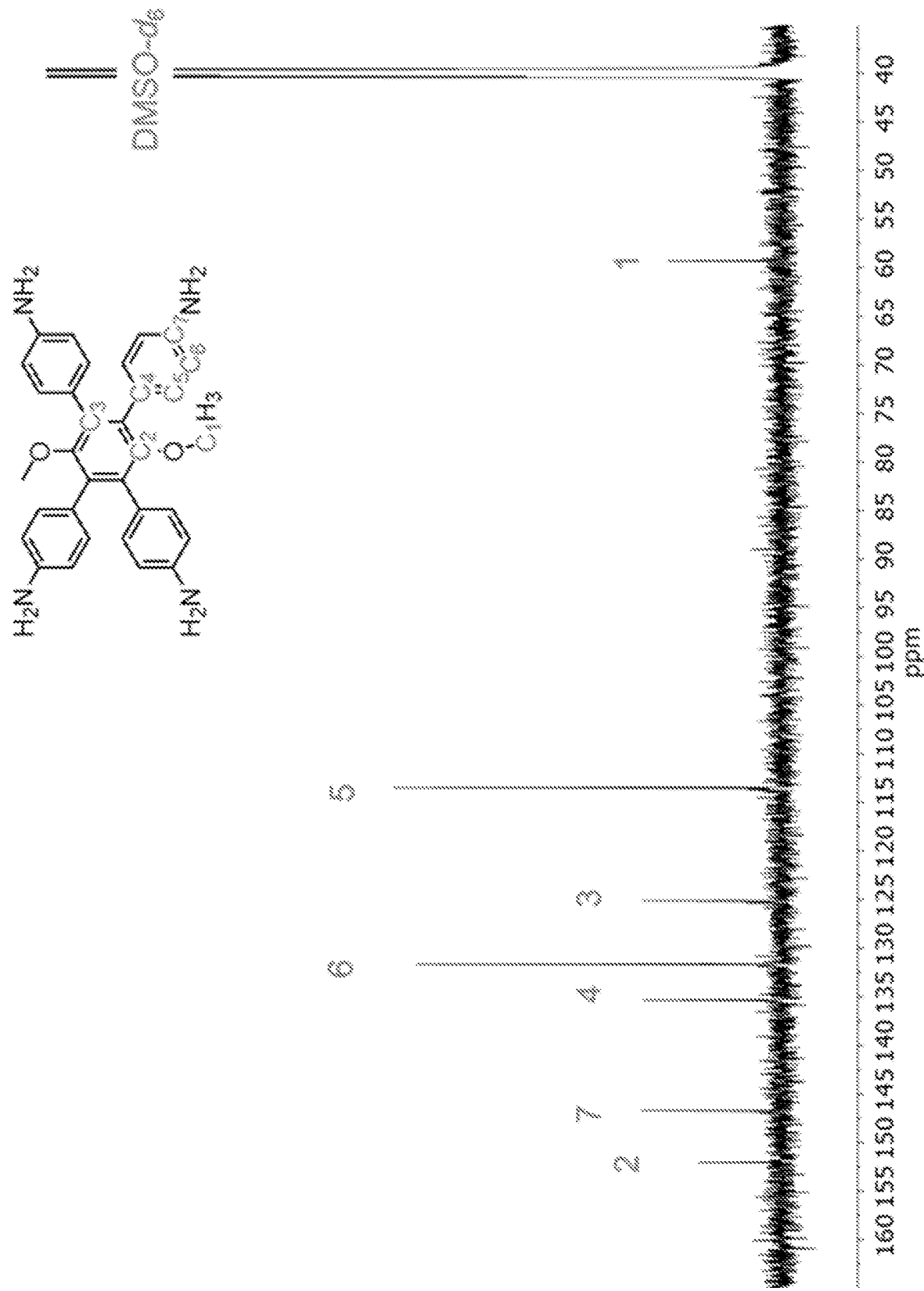


Figure 60

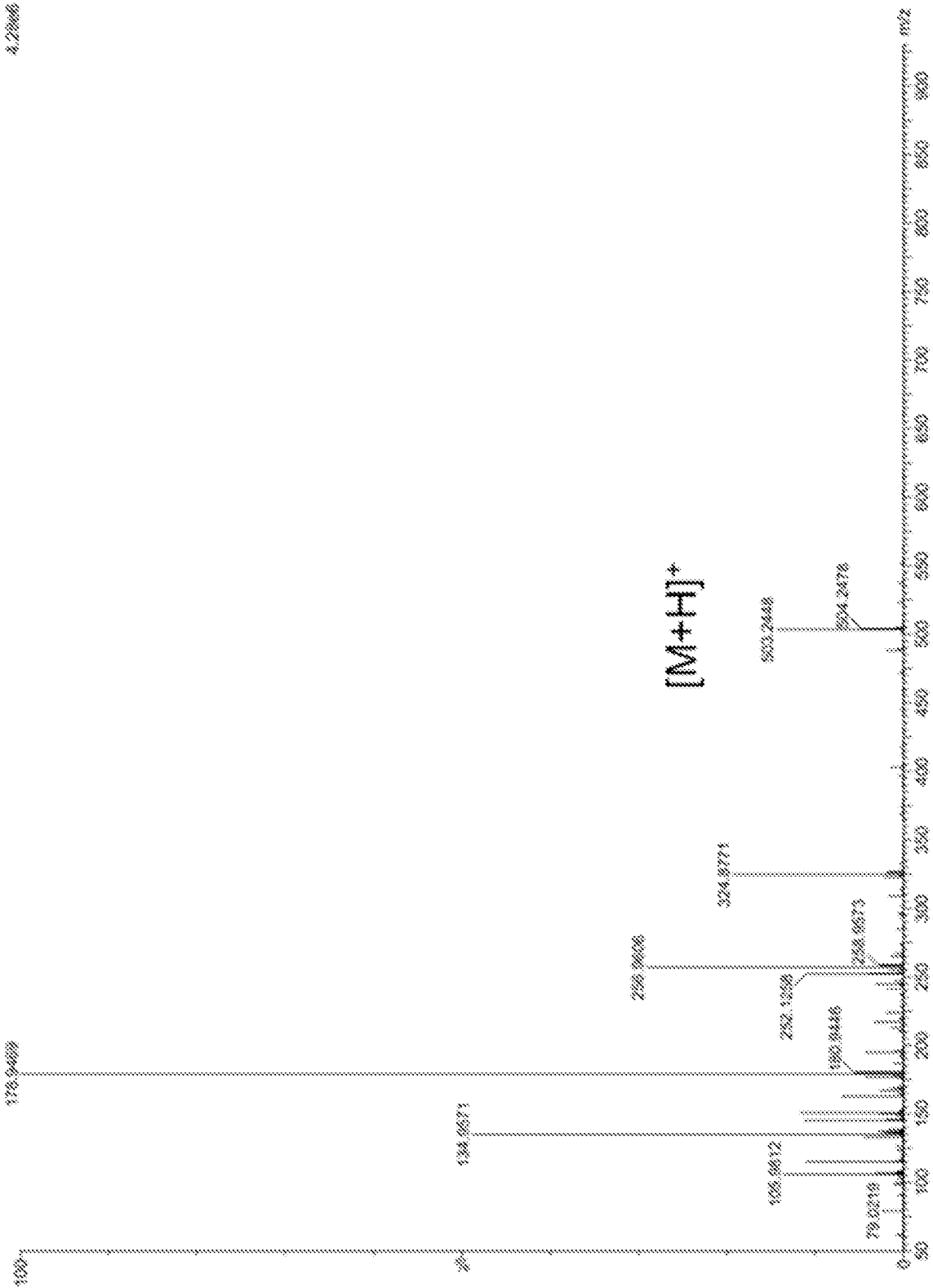


Figure 61

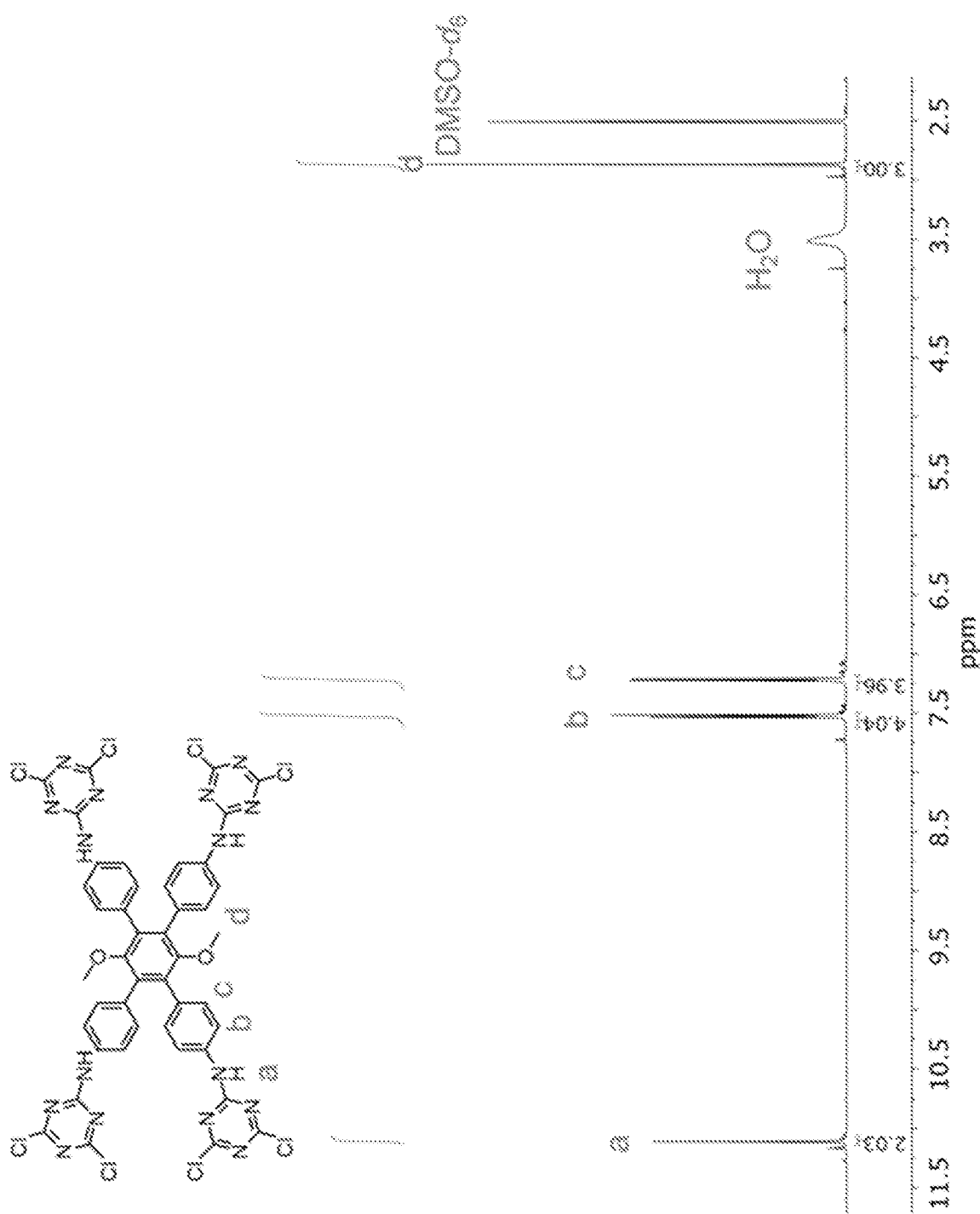


Figure 62

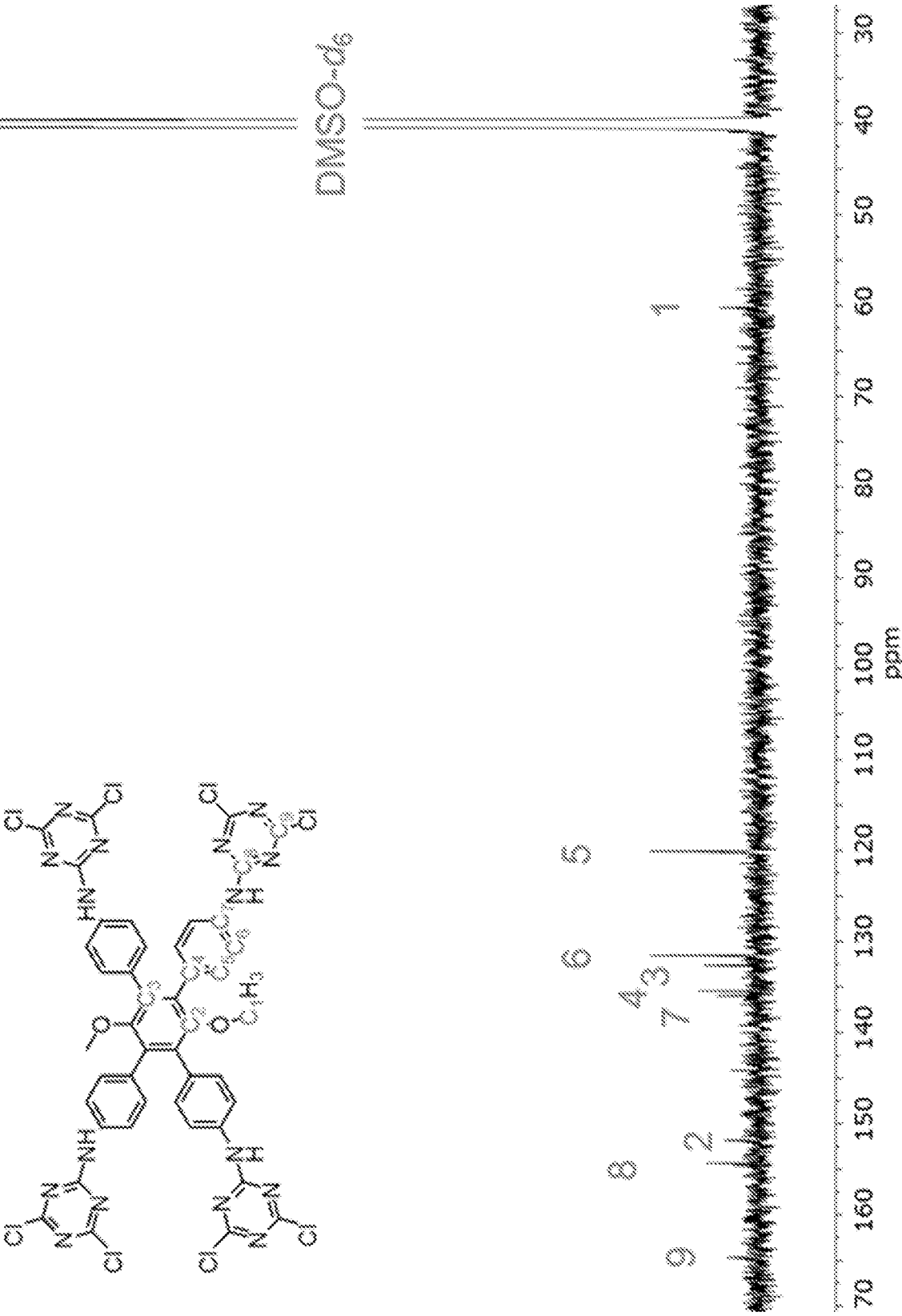


Figure 63

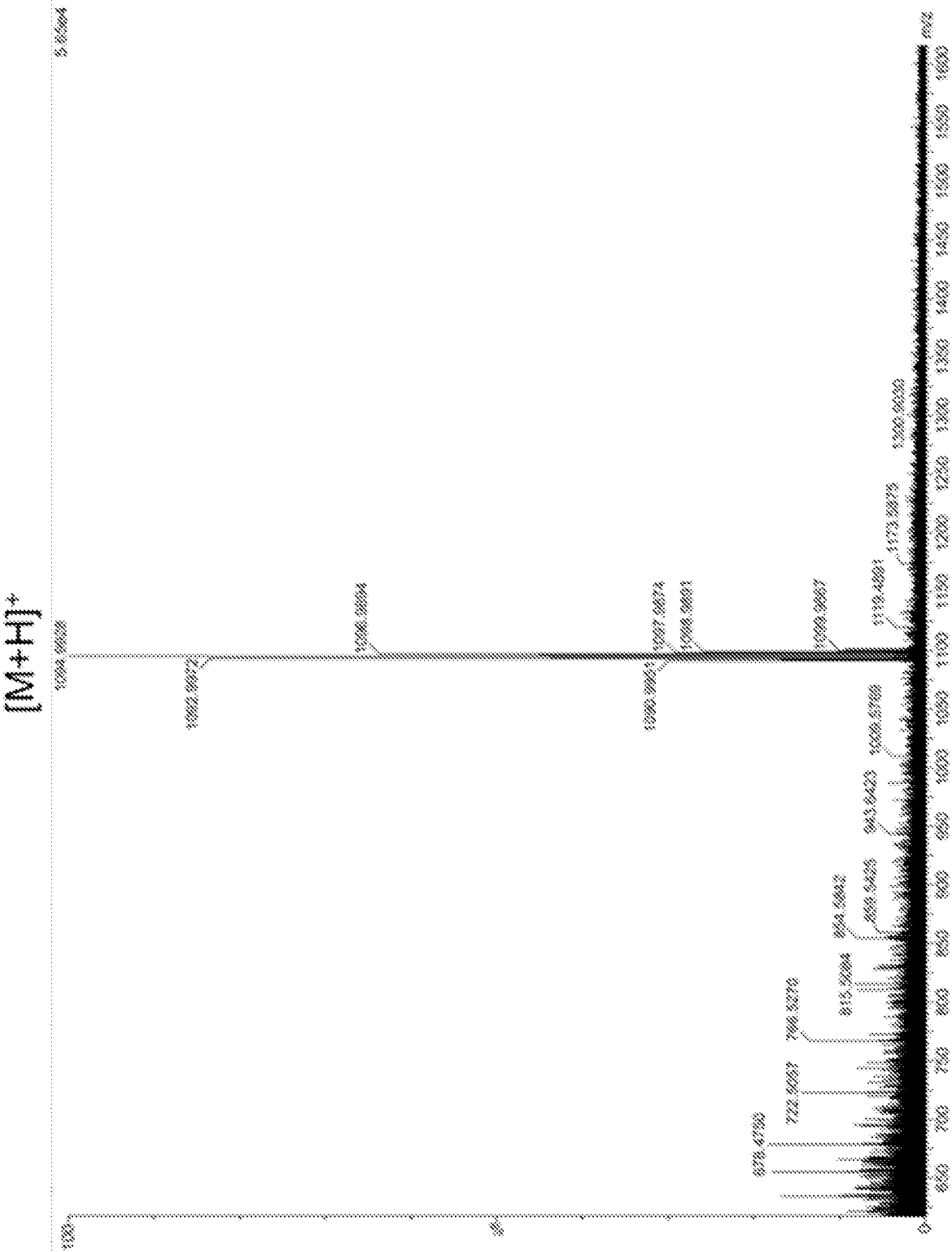


Figure 64

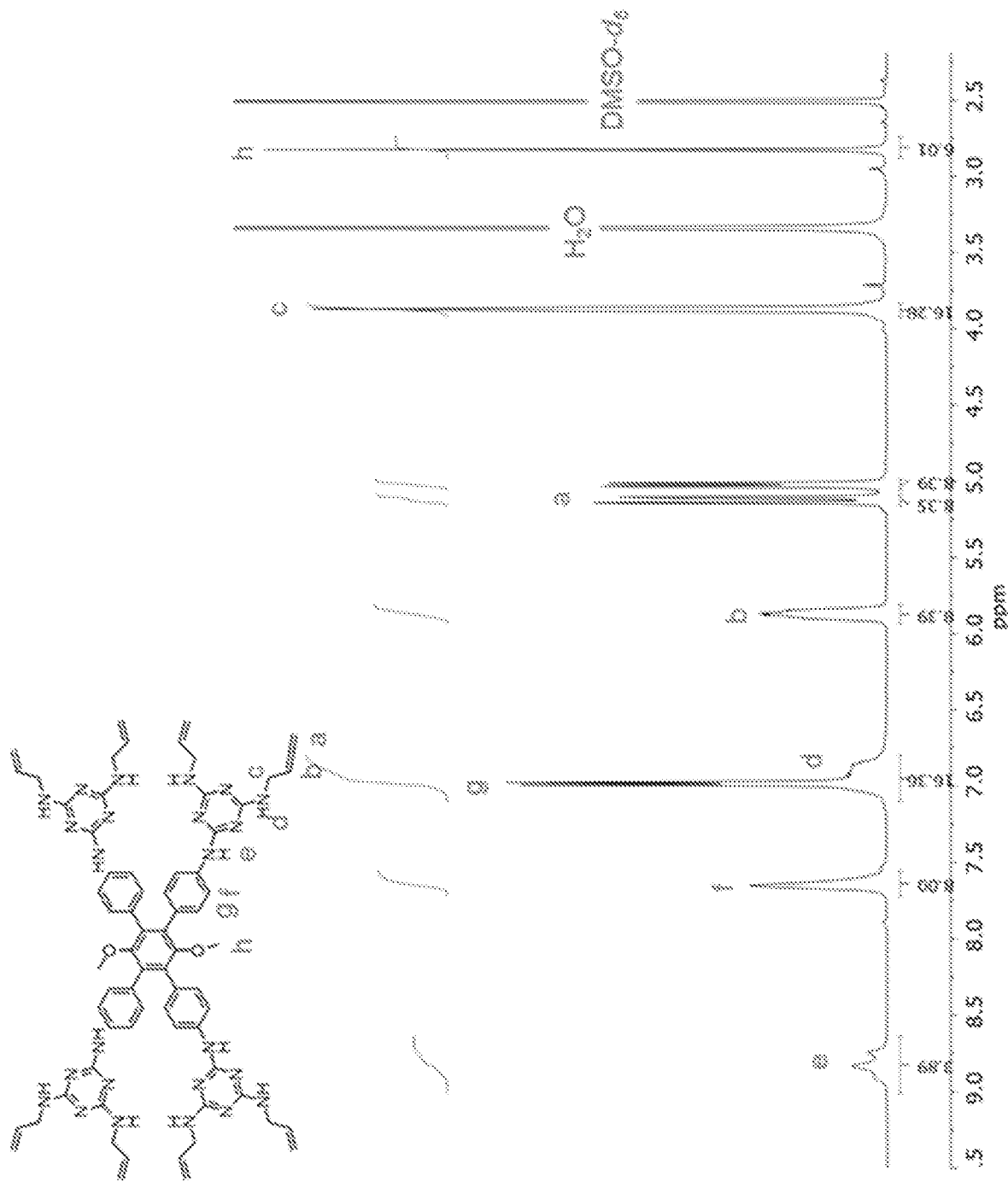


Figure 65

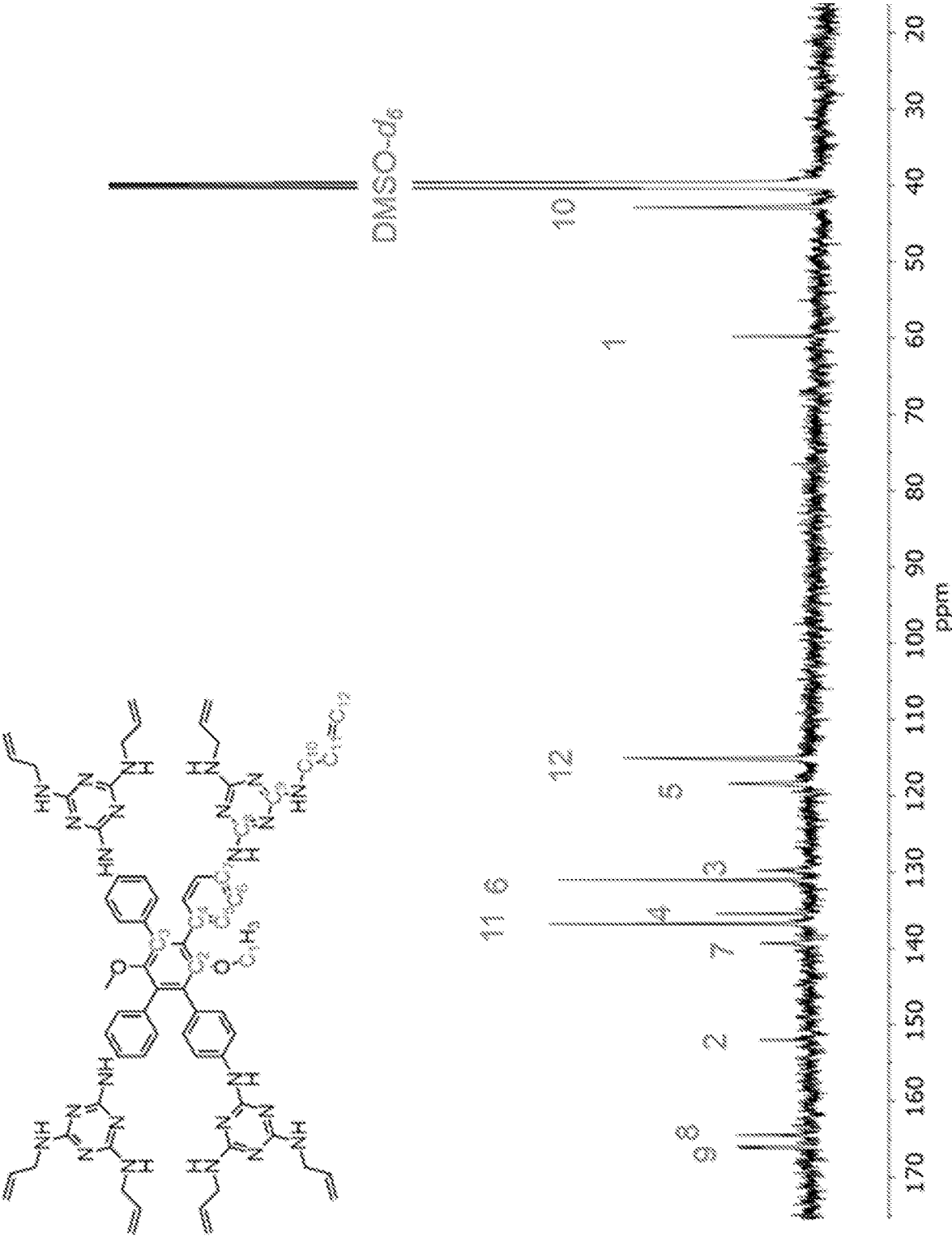


Figure 66

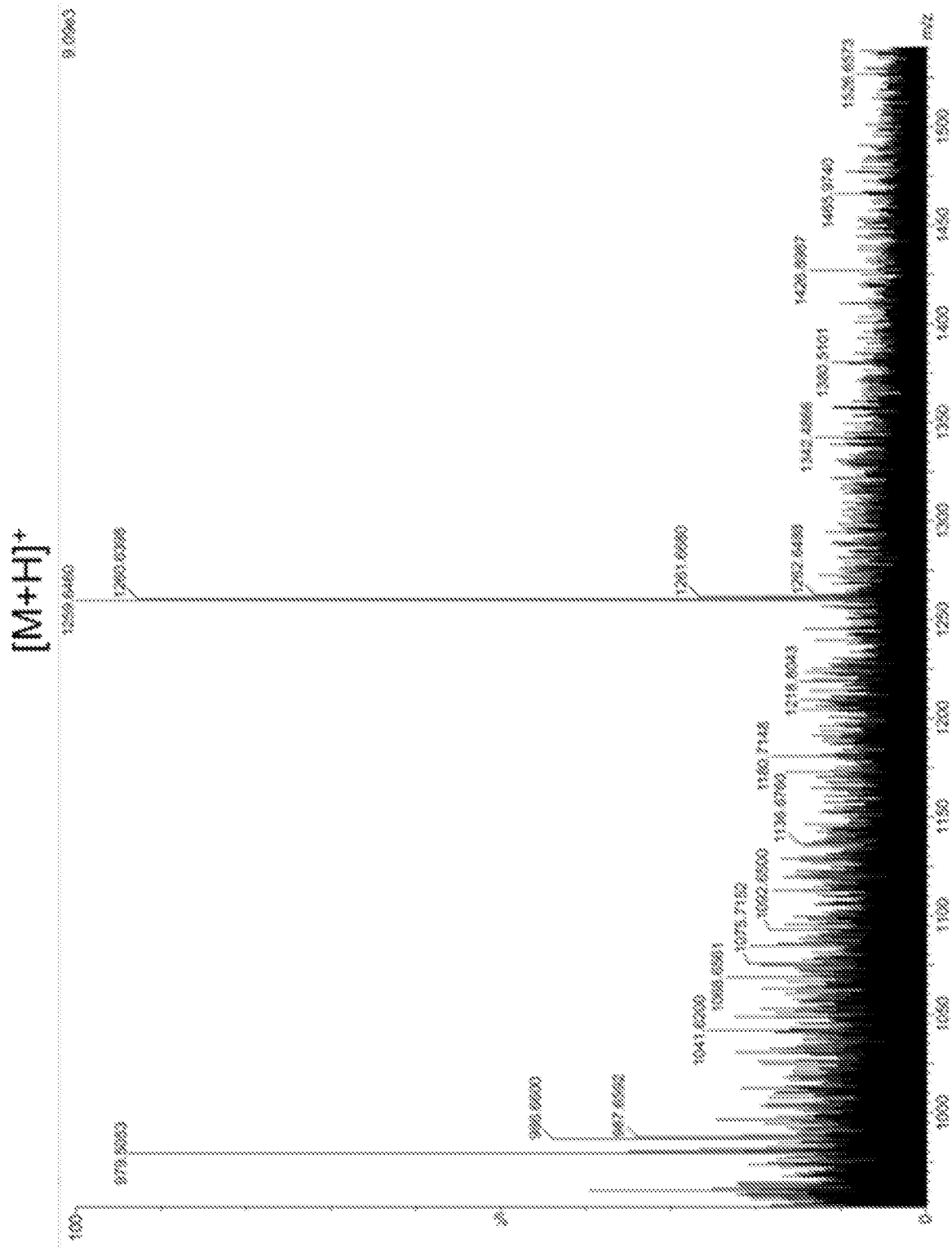


Figure 67



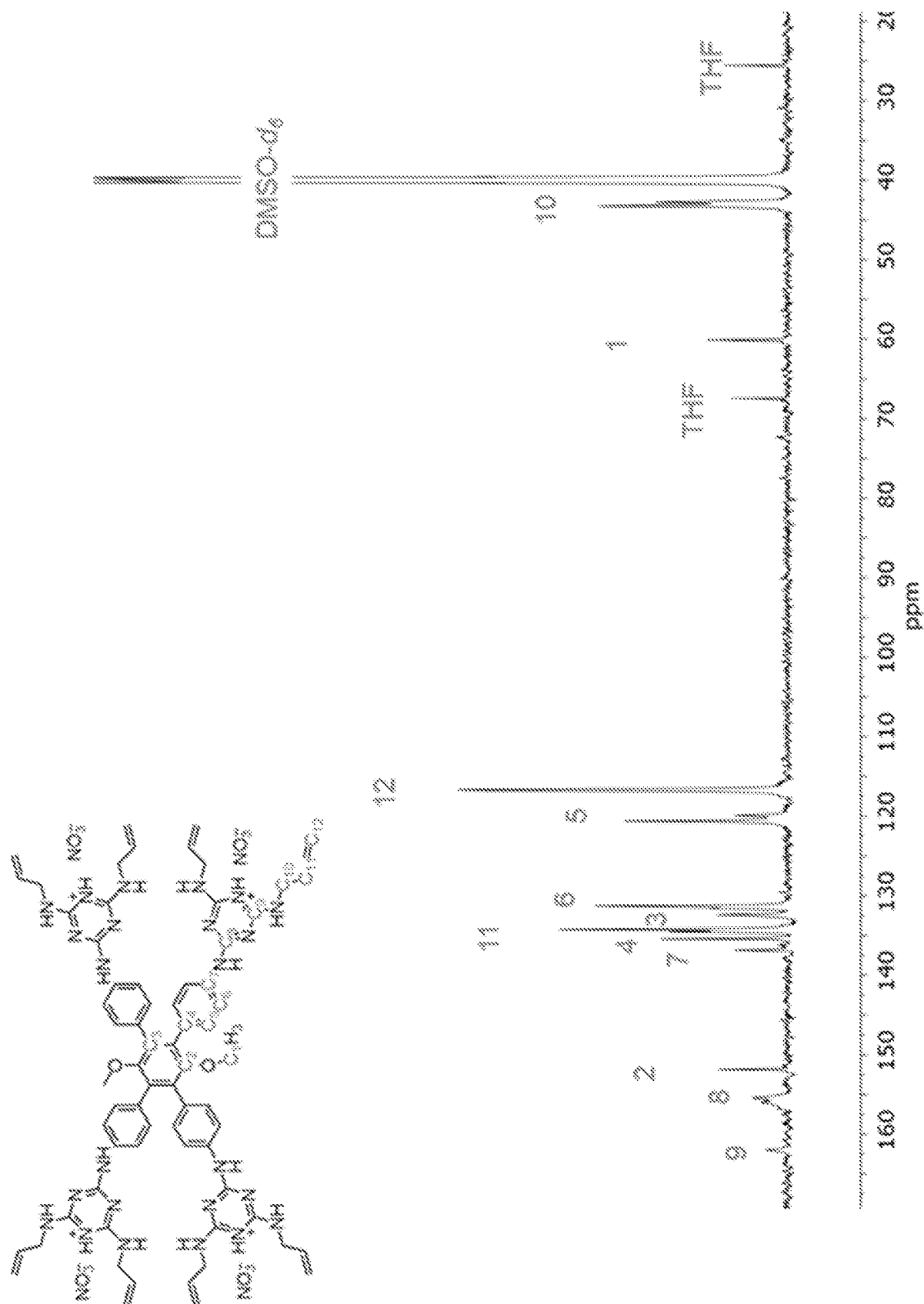


Figure 69

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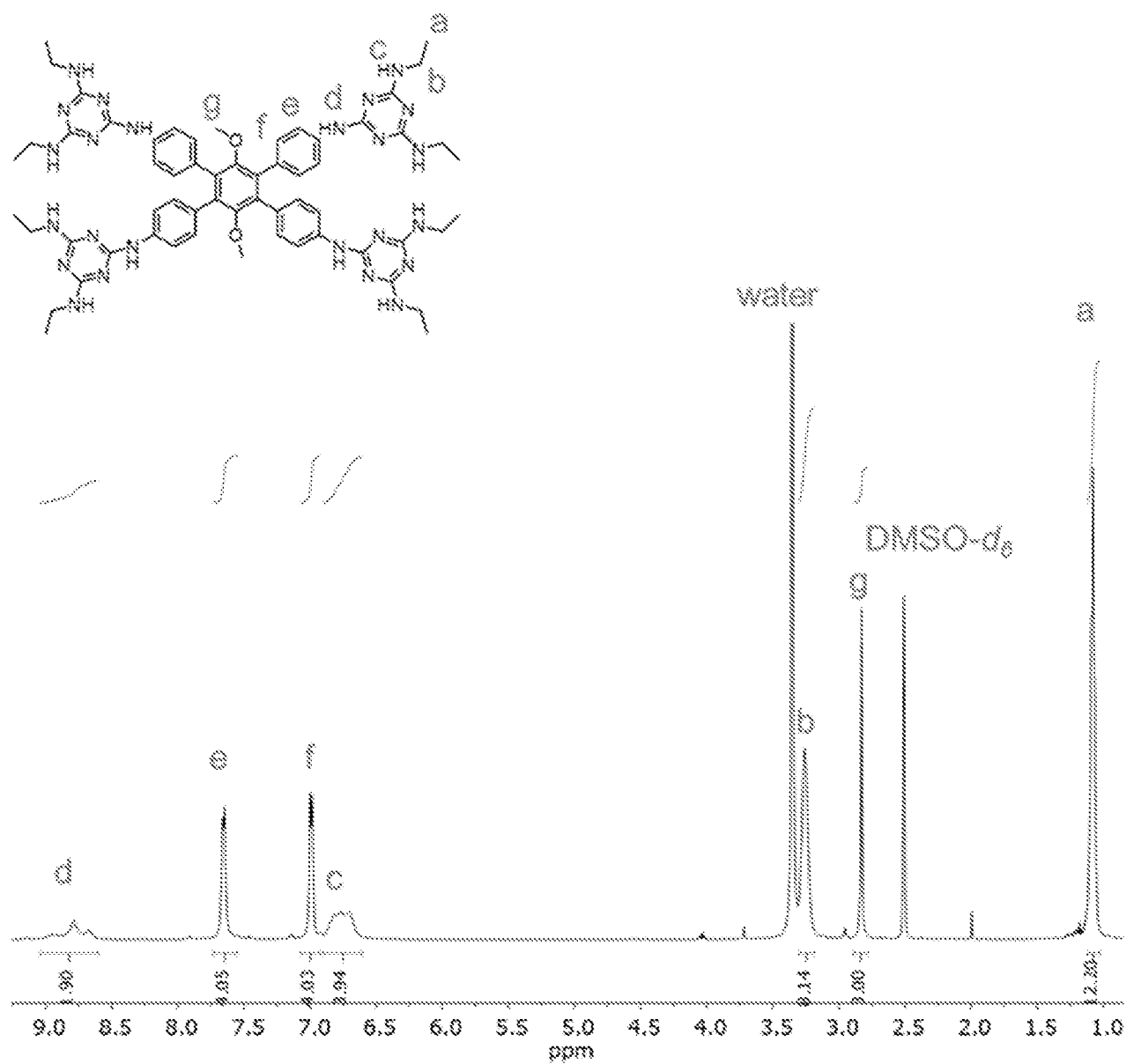


Figure 70

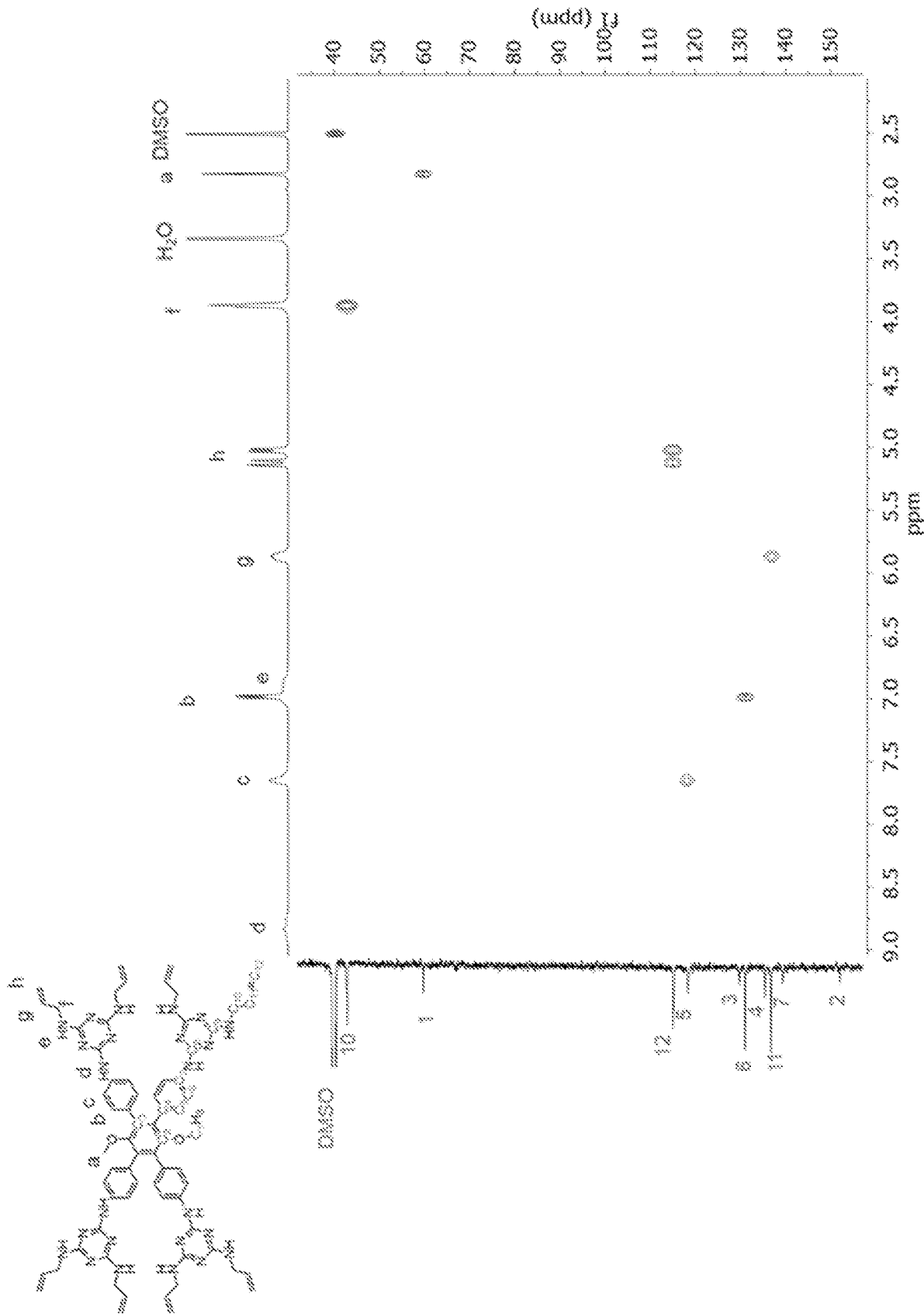


Figure 7I

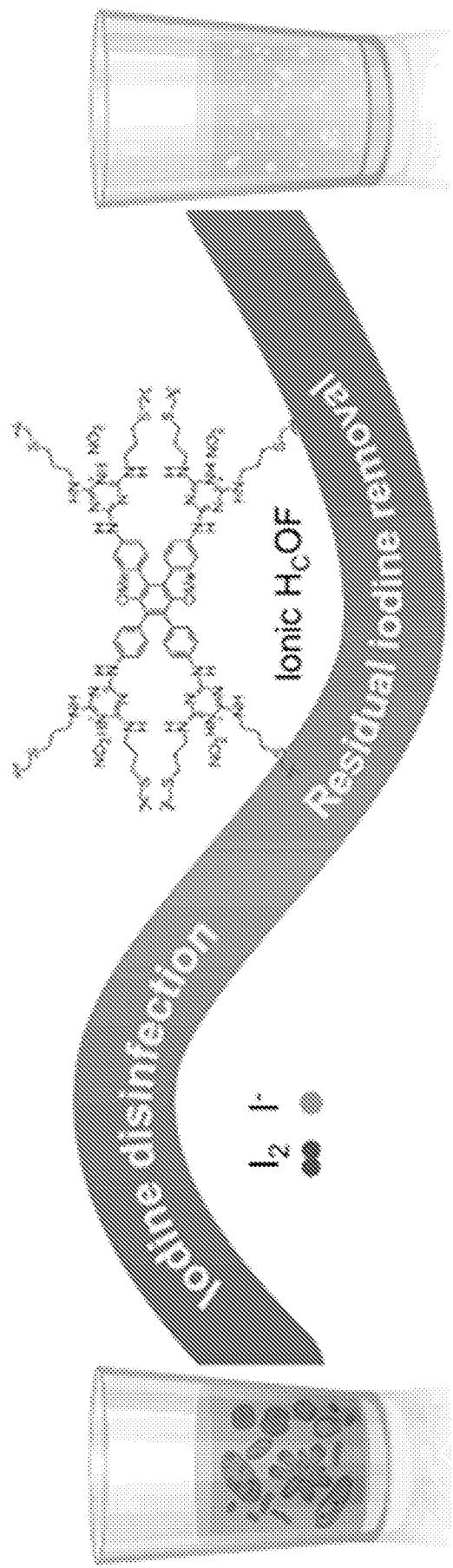


Figure 72

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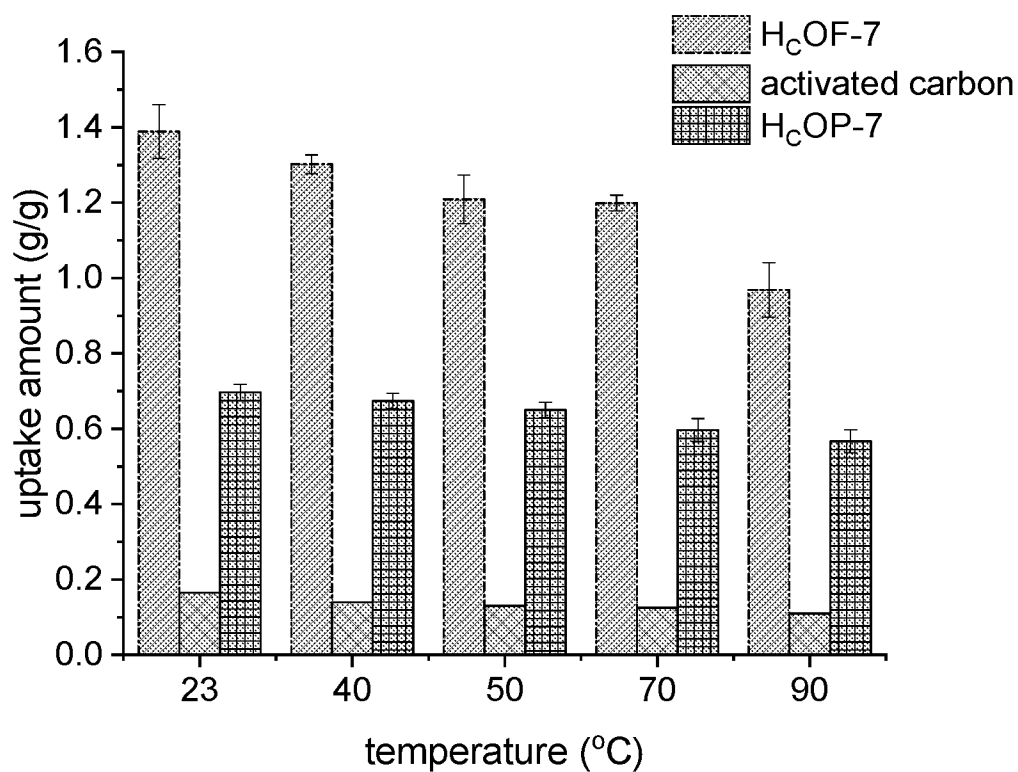


Figure 73

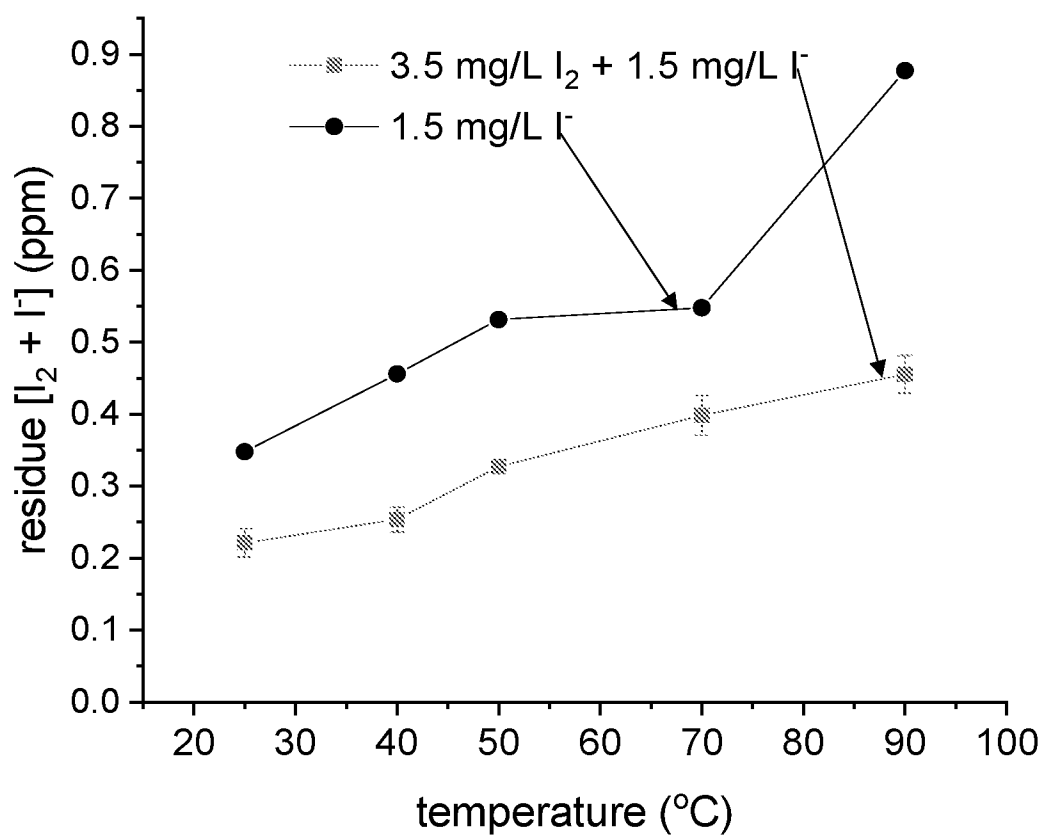


Figure 74

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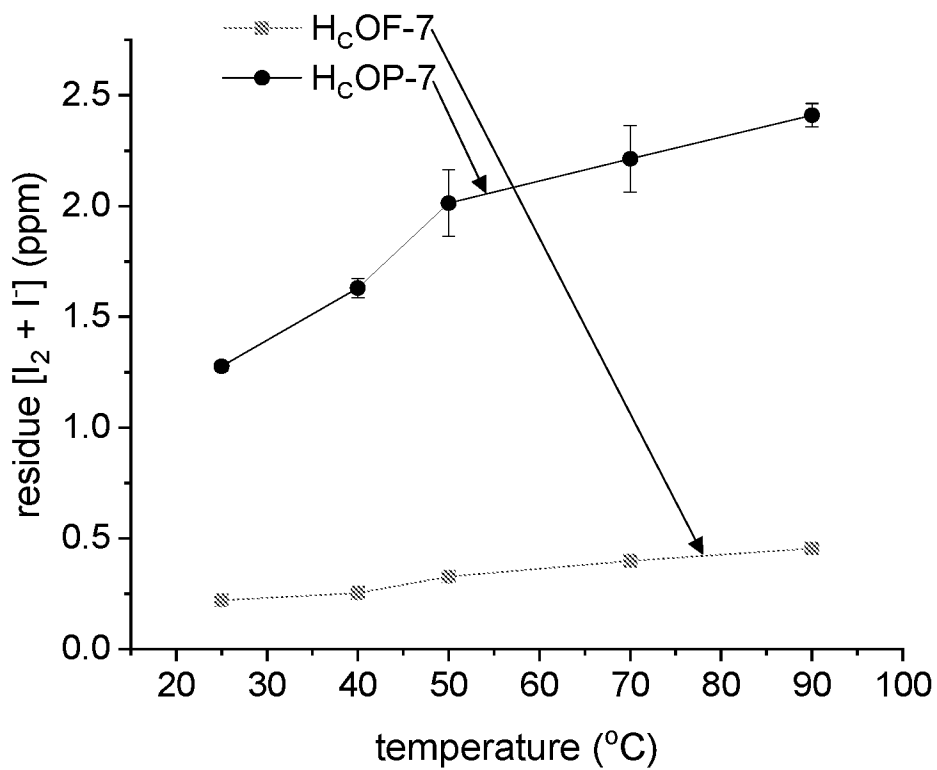


Figure 75

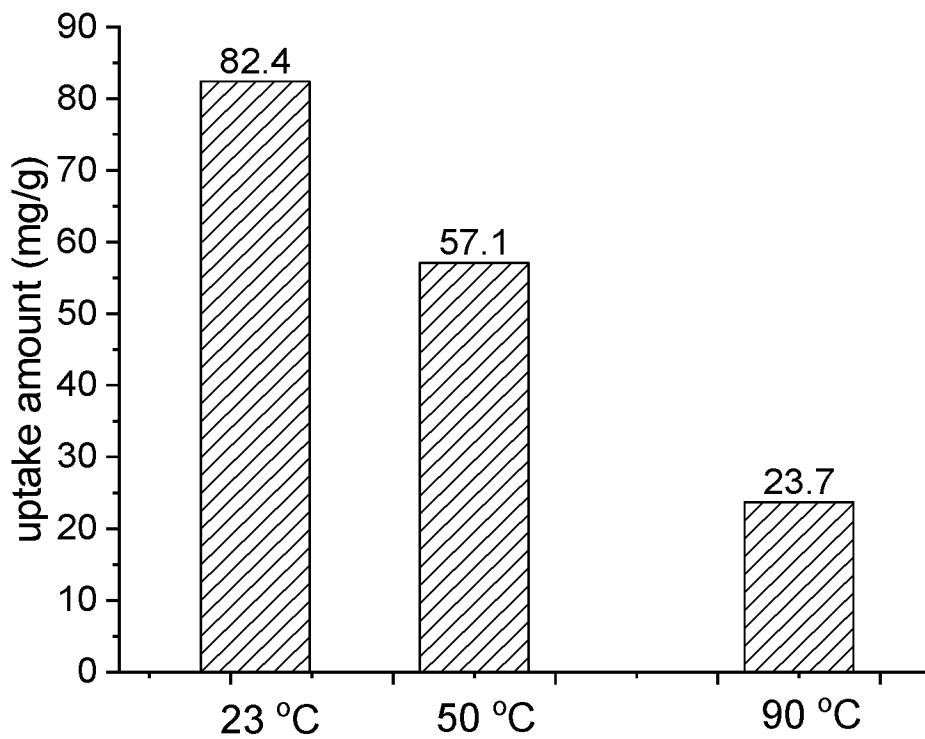


Figure 76

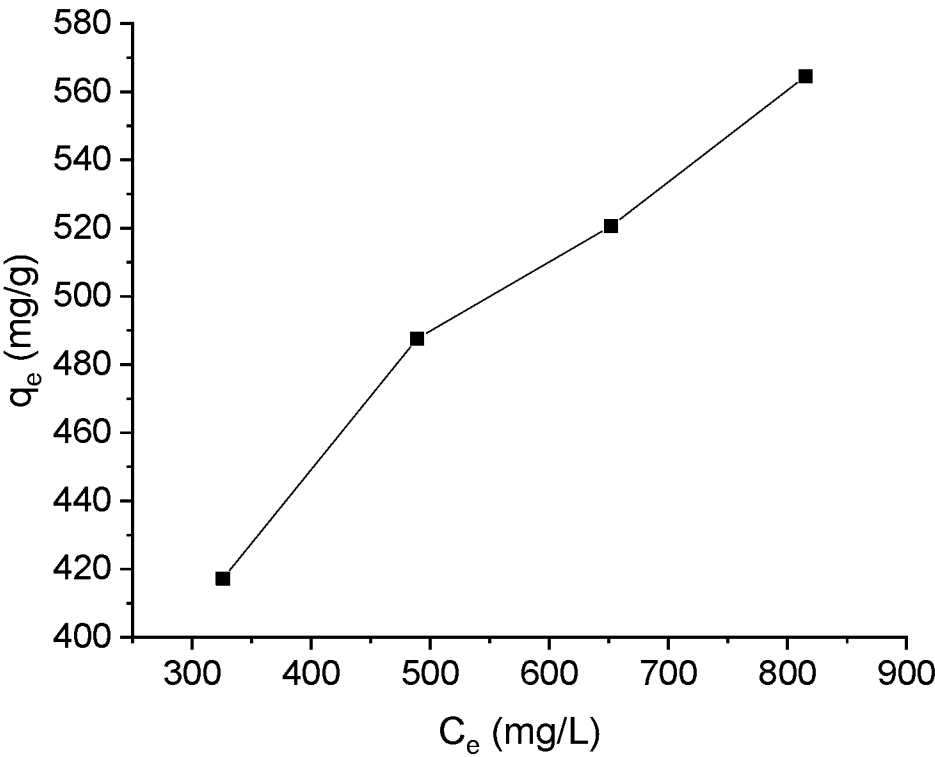


Figure 77

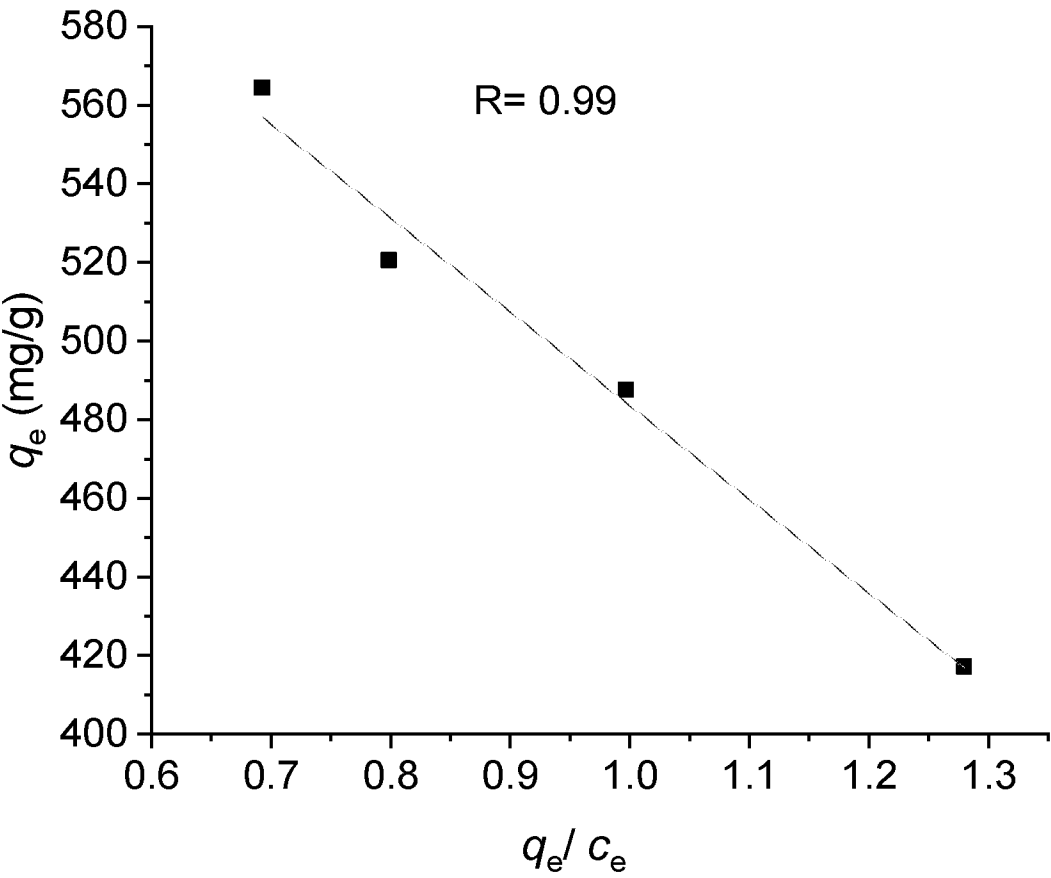


Figure 78

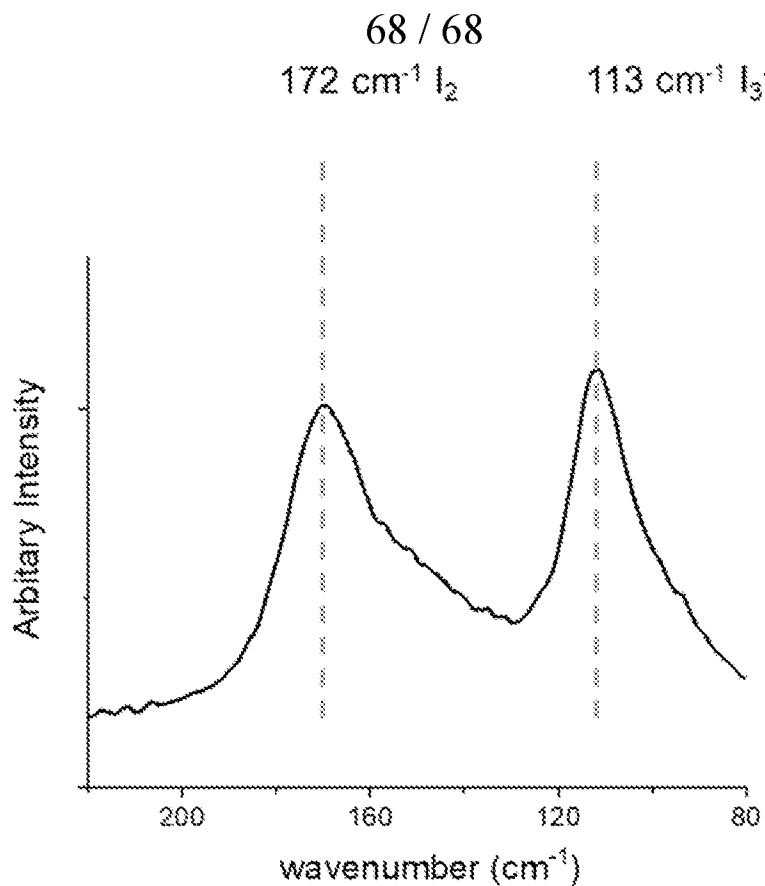


Figure 79

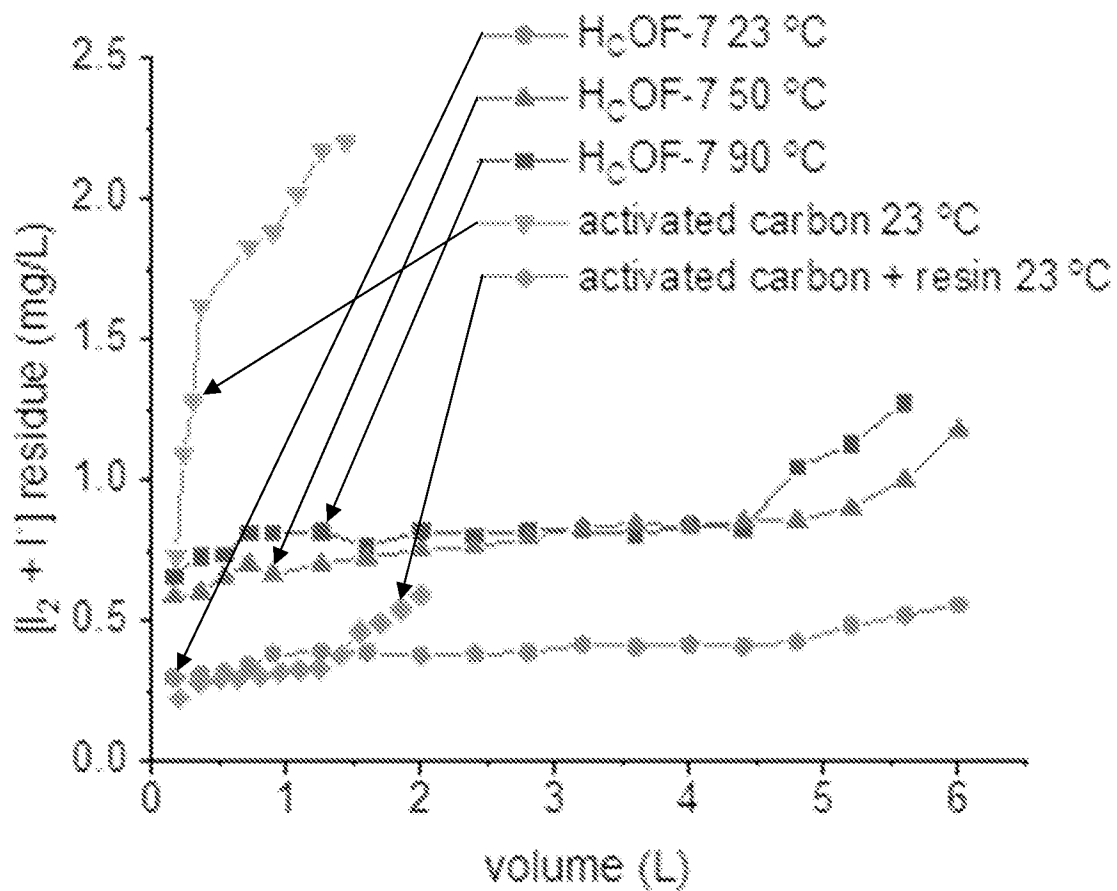


Figure 80