Electronic Supplementary Material (ESI) for Chemical Science.
This journal is © The Royal Society of Chemistry 2021

Electronic Supplementary Information

Precise Fabrication of Porous Polymer Frameworks Using Rigid Polyisocyanides as Building Blocks: from Structure Regulation to Efficient Iodine Capture

*Xun-Hui Xu, Yan-Xiang Li, Li Zhou, Na Liu, and Zong-Quan Wu**

Department of Polymer Science and Engineering, School of Chemistry and Chemical Engineering, and Anhui Key Laboratory of Advanced Catalytic Materials and Reaction Engineering, Hefei University of Technology, Hefei 230009, Anhui Province, China

Table of Contents

Measurements

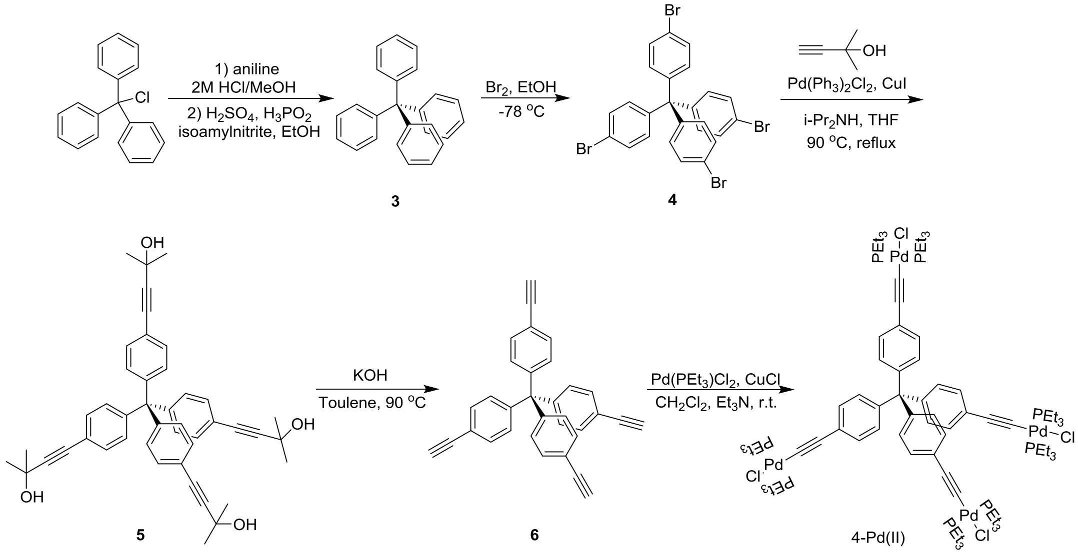
The NMR spectra were recorded using a Bruker 600 MHz spectrometer {H}. Size exclusion chromatography (SEC) was performed on Waters 1515 pump and Waters 2414 differential refractive index (RI) detector (set at 40 °C) using a series of two linear TSK gel GMHHR-H columns. Molecular weight (M_n) and its dispersity (M_w/M_n) were reported relative to polystyrene standards. The eluent was tetrahydrofuran (THF) at a flow rate of 0.8 mL/min. FT-IR spectra were recorded on Perkin-Elmer Spectrum BX FTIR system using KBr pellets. Circular dichroism (CD) spectra were obtained in a 1.0 or 0.1 cm quartz cell using a JASCO J1500 spectropolarimeter. The UV-vis absorption spectra were recorded on a UNIC 4802 UV/vis double beam spectrophotometer. The optical rotations were performed at 25 °C using a 10.0 cm quartz cell on a WZZ-2B polarimeter. Scanning electron microscopy (SEM) was performed on a SU8020 operating at 5.0 kV accelerating voltage. Nitrogen gas sorption experiments were carried out on Autosorb iQ Station 1 volumetric gas sorption instrument. Before measurement, the samples were degassed under vacuum at 80 °C for 12 h. The Brunauer Emmett-Teller (BET) method was utilized to calculate the specific surface areas. By using the nonlocal density functional theory (DFT) model, the pore volume was derived from the sorption curve. Differential scanning calorimetric (DSC) measurements were carried on a Mettler-Toledo DSC821e instrument. Samples were first heated from 0 to 140 °C at a heating rate of 5 °C/min under nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere at a heating rate of 5 °C/min from 30 to 800 °C using a Netzsch TG 209 F3 instrument. X-ray diffraction measurements were conducted by using a Bruker D8 advance X-ray powder diffractometer with CuKα (1.541 Å) radiation (40 kV, 40 mA) and samples were exposed at a scan rate of $2\theta = 0.02°/s$ in the range between 3° and 40°.

Materials

All solvents were obtained from Sinopharm. Co. Ltd., and were purified by the standard procedures before use. All chemicals were purchased from Aladdin, Sinopharm, and Sigma-Aldrich Chemical Co. Ltd., and were used as received without further purification otherwise denoted. The Pd(II) catalyst and the isocyanide monomer **1**, cross-linker **2**, and linear poly-$\mathbf{1}_5$ were prepared according to the procedures reported by our group previously, and the structure was confirmed by ^{1}H NMR,^{13}C NMR spectra, FT-IR and MS m/z.[1,2]

Synthetic procedures

Scheme S1. Synthesis of 4-Pd (II) Catalyst.



*Tetraphenylmethane (**3**):*[3] This compound was prepared followed the reported literature with slight modification.[4] In a round bottomed flask, chlorotriphenylmethane (13.02 g, 46.60 mmol, 1.0 equiv.) and aniline (10.0 mL, 10.23 g, 105.4 mmol, 2.3 equiv.) were heated at 190 °C under vigorous stirring. After 15 min, the reaction mixture was allowed to cool to room temperature. Then, an aqueous solution of HCl (2M, 80 mL) and methanol (50 mL) were added to the pulverized solid and the reaction mixture was heated for 30 min at 80 °C. After cooling to room temperature, the resulting solid was filtered off, washed with water (250 mL) and dried in *vacuo* (70 °C, 16 h).

The dry solid was suspended in EtOH (250 mL) and cooled to –20 °C. At this temperature, sulfuric acid (98%, 11 mL) and isoamylnitrite (8 mL) were added slowly and the suspension was stirred for 1 h. After this, hypophosphoric acid (30%, 20 mL) was added dropwise. Once the addition was completed, the reaction mixture was heated to 50 °C until the evolution of gas has ceased. Then, the solid was filtered off and washed subsequently with DMF (250 mL), water (250 mL) and EtOH (250 mL). This washing procedure was repeated twice. After drying in *vacuo* (70 °C, 18 h), compound **3** (13.52 g, 91% yield) was obtained as off-white powder. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) δ 7.06-7.17 (20 H, m, ArH).

*Tetrakis(4-bromophenyl)methane (**4**):*[3] To a three necked round bottomed flask containing bromine (90.00 g, 0.63 mol, 20 equiv.), compound **1** (10.01 g, 31.3 mmol, 1 equiv.) was added in small portions under vigorous stirring at room temperature. After the addition was completed, the resulting solution was stirred for 20 min and then cooled down to –78 °C. At this temperature, ethanol (150 mL) was added slowly and the formed suspension was allowed to warm to room temperature under stirring overnight. The precipitate was filtered off and washed subsequently with an aqueous sodium hydrogensulfite solution (100 mL) and water (100 mL). After drying in *vacuo*, compound **4** (16.0 g, 80% yield) was obtained as a yellowish solid. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) δ 7.42–7.38 (dd, J_1 = 6 Hz, J_2 = 6 Hz, 8H, ArH), 7.01–6.99 (dd, J_1 = 6 Hz, J_2 = 6 Hz, 8H, ArH).

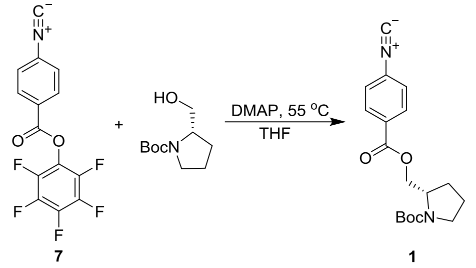
*(Trimethylsilylethynyl)phenyl)methane (**5**):*[3] In a round bottomed flask, tetrakis(4-bromophenyl)methane (1.51 g, 2.36 mmol, 1.0 equiv.) was dissolved in dry THF (10.0 mL) under argon atmosphere. To this solution, *i*-Pr_2NH (10.0 mL), 2-methyl-3-butyn-2-ol (2.58 g, 30.6 mmol, 13.0 equiv.), bis(triphenylphosphine)palladium chloride (0.06 g, 0.24 mmol, 0.1 equiv.) and cuprous(I) iodide (20 mg, 0.16 mmol, 0.07 equiv.) were added subsequently. The resulting suspension was heated at 80 °C for 24 h. Then, the volatiles were removed by evaporation under reduced pressure. The residue was taken up in diethylether (50 mL) and aqueous solution of HCl (2M, 20 mL). The organic phase was separated, washed with water (20 mL) and dried over sodium sulfate. After removing of the solvent under reduced pressure, the afforded crude product **5** was directly used for next step without further purification.

*Tetrakis(4-ethynylphenyl)methane (**6**):*[3] Compound **5** (0.54 g, 0.75 mmol, 1.0 equiv.), potassium hydroxide (0.21 g, 3.75 mmol, 5 equiv.) and toluene (20 mL) were added to a round bottom flask under a nitrogen atmosphere. After stirred at 80 °C for 30 min, the reaction mixture was diluted with water (25 mL) and extracted three times with CH_2Cl_2 (20 mL). The combined organic phase was washed with saturated aq. $NaHCO_3$ (10 mL × 2) and brine (10 mL × 1) and dried over magnesium sulfate. After the solvent was removed by evaporation under reduced pressure, the crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate, v/v = 10/1). Compound **6** was obtained (0.26 g, 77% yield over two steps) as a yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) δ 7.40–7.38 (d, J = 12 Hz, 8 H, ArH), 7.13–7.11 (d, J = 12 Hz, 8 H , ArH), 3.06 (s, 4 H, C≡CH).

4-Pd(II) Catalyat:[1] Compound **6** (200 mg, 0.49 mmol), *trans*-dichlorobis(triethylphosphine)palladium (820 mg, 2.0 mmol), and cuprous(I) chloride (2.5 mg, 0.025 mmol) were dissolved in the mixture of triethylamine (10 mL) and dichloromethane (10 mL) under dry nitrogen atmosphere. The mixture was stirred at room temperature for 2 h, then the solvent was removed by evaporation under reduced pressure. The afforded residue was purified by chromatography using petroleum ether as eluent. The crude product was recrystallized from petroleum ether and methanol to afford the expected 4-Pd(II) catalyst as a white solid (613 mg, 60% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.11–7.10 (d, J = 6 Hz, 8H, ArH), 7.06–7.05 (d, J = 6 Hz, 8H, ArH), 1.99–1.97 (m, 12H, CH_2), 1.21–1.16 (m, 18H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 144.1, 130.7, 129.8, 125.2, 106.0, 95.2, 64.3, 15.3, 8.3. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 18.4. FT-IR

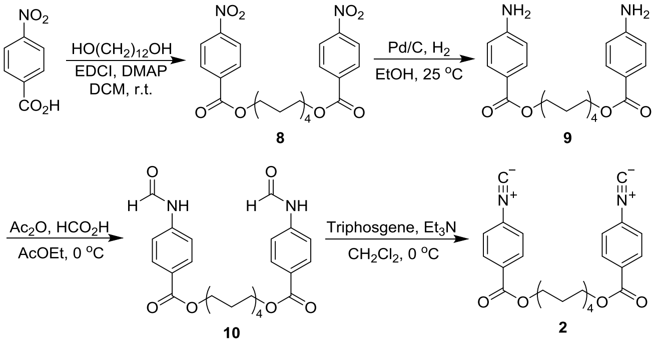
(KBr, 25 °C, cm^{-1}): 2961 ($\nu_{Ar\text{-}H}$), 2931 ($\nu_{Ar\text{-}H}$), 2876 ($\nu_{C\text{–}H}$), 2179 ($\nu_{C\equiv C}$), 1727 ($\nu_{C=C,\ Ar}$), 1648 ($\nu_{C=C,\ Ar}$). MS m/z calcd for $C_{81}H_{137}Cl_4P_8Pd_4$ [M + H]$^+$: 1925.35; Found: 1925.30. Anal. Calcd (%) for $C_{81}H_{136}Cl_4P_8Pd_4$: C, 50.53; H, 7.12. Found: C, 50.49%; H, 7.17%.

Scheme S2. Synthesis of Monomer **1**



Monomer 1:[2] This compound was synthesized according to Scheme S2. Phenyl isocyanide (**7**) carrying pentafluorophenol ester was first prepared followed the procedure reported by our group previously and the structure was confirmed by ^{1}H NMR.[4] A mixed solution of monomer **7** (4.82 g, 15.2 mmol), *tert*-butyl-(*S*)-2-(hydroxymethyl)pyrrolidine-1-carboxylate (3.02 g, 15.4 mmol), and 4-*N,N*-dimethylaminopyridine (DMAP, 1.36 g, 11.2 mmol) in dry THF (20 mL) was stirred at 55 °C for 12 h under dry nitrogen. Then the solvent was removed by evaporation under reduced pressure. The residue was re-dissolved in CH_2Cl_2 (25 mL) and washed with water (50 mL × 2) and an aqueous solution of sodium bicarbonate ($NaHCO_3$, 50 mL × 2). The organic layer was dried over magnesium sulfate ($MgSO_4$) and purified by flash column chromatography using petroleum ether and ethyl acetate as eluent (v/v = 8/1) to afford monomer **1** as a colorless oil (4.32 g, 87% yield). ^{1}H NMRd (600 MHz, $CDCl_3$, 25 °C): δ 8.08–8.06 (d, J = 12.0 Hz, 2H, ArH), 7.44–7.42 (d, J = 12.0 Hz, 2H, ArH), 4.40–4.24 (m, 2H, OCH_2), 4.09 (m, 1H, NCH), 3.46–3.38 (m, 2H, NCH_2), 1.92–1.73 (m, 4H, CH_2), 1.44 (s, 9H, CH_3). FT-IR (KBr, 25 °C, cm^{-1}): 2975 ($\nu_{C\text{-}H}$), 2935 ($\nu_{C\text{-}H}$), 2122 ($\nu_{C\equiv N}$), 1726 ($\nu_{C=O}$), 1691 ($\nu_{C=O}$).

Scheme S3. Synthesis of Cross-linker **2**



*Dodecane-1,12-diyl bis(4-nitrobenzoate) (**8**):*[5] 4-Dimethylaminopyridine (DMAP) (4.80 g, 39.3 mmol) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI) (13.00 g, 68.0 mmol) were added to a solution of 4-nitrobenzoic acid (9.90 g, 59.3 mmol) in dry CH_2Cl_2 (150 mL). After the reaction mixture was stirred at 0 °C for 30 min under an atmosphere of nitrogen, dodecane-1,12-diol (5.00 g, 24.7 mmol) was added to the mixture. The dispersion was stirred at room temperature for 5 h. After filtered the resulting reaction mixture, the residual solvent was removed by evaporation. The crude product was purified by column chromatography using ethyl acetate and petroleum ether (v/v = 1/4) as eluent to afford compound **8** as a colorless solid (11.20 g, 91% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.28–8.26 (d, J = 6 Hz, 4H, ArH), 8.21–8.20 (d, J = 6 Hz, 4H, ArH), 4.36 (t, J = 6 Hz, 4H,CO_2CH_2), 1.80–1.25 (m, 20H, CH_2). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 164.7, 150.4, 135.8, 130.6, 123.5, 66.1, 29.7, 29.5, 29.2, 28.6, 25,9. FT-IR (KBr, 25 °C, cm^{-1}): 2961 ($\nu_{Ar\text{-}H}$), 2931 ($\nu_{Ar\text{-}H}$), 2876 ($\nu_{C\text{-}H}$), 1721 ($\nu_{C=O}$), 1540 (ν_{asNO2}). MS m/z calcd. for $C_{26}H_{33}N_2O_8$ $[M + H]^+$: 501.22; Found: 501.19. Anal. Calcd (%) for $C_{26}H_{32}N_2O_8$: C, 62.39; H, 6.44; N, 5.60. Found: C, 62.35%; H, 6.48%; N, 5.57%.

*Dodecane-1,12-diyl bis(4-aminobenzoate) (**9**):* A solution of **8** (5.00 g, 16.3 mmol) in ethanol (150 mL) was charged with 10% Pd/C (0.30 g). The resulting mixture was stirred at room temperature for 9 h under an atmosphere of hydrogen. Following filtration through celite, the filtrate was concentrated by evaporation. The crude product was then purified by recrystallization from *n*-hexanes and ethyl acetate (v/v = 10/1) to afford the compound **9** as a white crystalline solid (4.16 g, 91% yield). ^{1}H NMR (600 MHz, DMSO-d_6, 25 °C): δ 7.61–7.59 (d, J = 12 Hz, 4H, ArH), 6.54–6.53 (d, J = 6 Hz, 4H, ArH), 5.90 (s, 4H, NH_2). 4.11 (t, J = 6 Hz, 4H, CO_2CH_2), 1.60 (m, 4H, CH_2). 1.37–1.16 (m, 16H, CH_2). ^{13}C NMR (150 MHz, DMSO-d_6, 25 °C): δ 166.3, 153.8, 131.4, 116.5, 113.1, 63.9, 29.4, 29.1, 25.9. FT-IR (KBr, cm^{-1}): 3429 ($\nu_{N–H}$), 2961 ($\nu_{Ar\text{-}H}$), 2931 ($\nu_{Ar\text{-}H}$), 2876 ($\nu_{C–H}$), 1727 ($\nu_{C=C,\ Ar}$), 1648 ($\nu_{C=C,\ Ar}$). MS m/z calcd for $C_{26}H_{37}N_2O_4$ $[M + H]^+$: 441.27; Found: 441.26. Anal. Calcd (%) for $C_{26}H_{36}N_2O_4$: C, 70.88; H, 8.24; N, 6.36. Found: C, 70.84%; H, 8.29%; N, 6.32%.

Compound 10: After a mixture of formic acid (10.6 mL, 280.00 mmol) and acetic anhydride (5.3 mL, 46.00 mmol) was stirred at room temperature for 1 h under dry nitrogen, compound **9** (5.00 g, 11.4 mmol) in dry ethyl acetate (120 mL) was added to the mixture at 0 °C *via* a syringe. The dispersion solution was stirred at 0 °C for 30 min, and then at room temperature for 2 h. The resulting solution was diluted with ethyl acetate (100 mL), washed with H_2O (20 × 2 mL) and brine (20 × 2 mL) and then dried over anhydrous Na_2SO_4. The solvent was removed by evaporation under reduced pressure. The obtained white powdery solid was washed three times with a large amount of saturated $NaHCO_3$ solution, and then the white solid was collected by filtration. The afforded compound **10** was directly used in the next step without further purification and characterization.

Compound 2: Triethylamine (2.3 mL, 16.6 mmol) was added to a solution of **10** (2.00 g, 4.01 mmol) in dry CH_2Cl_2 (40 mL). After the reaction mixture was stirred at 0 °C for 10 min under dry nitrogen, a solution of triphosgene (1.35 g, 4.48 mmol) in CH_2Cl_2 (20 mL) was added dropwise using a syringe to the mixture. The dispersion solution was stirred at room temperature for 1 h and then CH_2Cl_2 (50 mL) was added. After filtration, the solution was washed with aqueous $NaHCO_3$ (20 × 2 mL), saturated brine (20 × 2 mL) and dried over anhydrous Na_2SO_4. The solvent was removed by evaporation under reduced pressure and the crude product was purified by column chromatography with petroleum ether and ethyl acetate (v/v = 4/1) as eluent to afford **2** as a white solid (1.50 g 81% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.09–8.07 (d, J = 12 Hz, 4H, ArH), 7.45–7.44 (d, J = 6 Hz, 4H, ArH), 4.32 (t, J = 6 Hz, 4H, CO_2CH_2), 1.77–1.28 (m, 20H, CH_2). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 166.9, 165.1, 131.3, 130.8, 126.4, 109.9, 65.7, 29.5, 29.2, 28.6, 25.9. FT-IR (KBr, 25 °C, cm^{-1}): 2961 ($\nu_{Ar-H,}$), 2931 (ν_{Ar-H}), 2876 (ν_{C-H}), 2148 ($\nu_{C\equiv N}$), 1740 ($\nu_{C=O}$). MS m/z calcd for $C_{28}H_{37}N_2O_4$ $[M + H]^+$: 461.24; Found: 461.24. Anal. Calcd (%) for $C_{26}H_{36}N_2O_4$: C, 73.02; H, 7.00; N, 6.08. Found: C, 72.98%; H, 7.05%; N, 6.04%.

Typical procedure for 4-poly-1$_m$s: These polymers were prepared according to Scheme 1 in the main text. Taking 4-poly-$\mathbf{1}_{200}$ as an example. A 10 mL oven-dried flask was charged with monomer **1** (0.20 g, 0.61 mmol), 4-Pd(II) catalyst (1.50 mg, 7.59×10^{-4} mmol), dry $CHCl_3$ (3.0 mL) and a stir bar. The concentrations of monomer **1** and the Pd(II) complex were 0.2 and 0.001 M, respectively ($[\mathbf{1}]_0/[Pd]_0 = 200$). The reaction flask was then immersed into an oil bath at 55 °C and stirred overnight. After cooled to room temperature, the polymerization solution was precipitated into a large amount of *n*-hexane, collected by centrifugation, and dried in vacuum at room temperature overnight to afford 4-poly-$\mathbf{1}_{200}$ as a brown solid (0.16 g, 80% yield). $[\alpha]^{25}_D = -221$ (c = 0.20, THF). SEC: M_n = 73.5 kDa, M_w/M_n = 1.20. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.41 (br, 2H, ArH), 5.70 (br, 2H, ArH), 3.92 (br, 3H, OCH_2 and NCH), 3.36 (br, 2H, NCH_2), 1.75 (br, 4H, $(CH_2)_2$), 1.41 (br, 9H, CH_3). FT-IR (KBr, 25 °C, cm^{-1}): 2985 (ν_{C-H}), 1722 ($\nu_{C=O}$), 1600 ($\nu_{C=N}$).

Typical procedure for C-poly-1$_m$s: These polymers were prepared according to Scheme 1 in the main text. Taking C-poly-$\mathbf{1}_{200}$ as an example. A 10 mL oven-dried flask was charged with 4-poly-$\mathbf{1}_{200}$ (0.16 g), linker **2** (0.18 mg, 3.9×10^{-4} mmol), dry $CHCl_3$ (2.00 mL) and a stir bar. The reaction flask was then immersed into an oil bath at 55 °C and stirred overnight. After cooled to room temperature, the polymerization solution was precipitated into a large amount of methanol, the precipitated solid was collected by centrifugation, and dried in vacuum at room temperature overnight to afford C-poly-$\mathbf{1}_{200}$ as a brown solid (157 mg, 98% yield). After dissolving the collected polymer in benzene (10.0 mL), it was freeze-dried for 24 hours, and afforded the desired C-poly-$\mathbf{1}_{200}$. $[\alpha]^{25}_D$ = –230 (c = 0.20, THF). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.47 (br, 2H, ArH), 5.86 (br, 2H, ArH), 4.03 (br, 3H, $CHCH_2$), 3.36 (br, 2H, NCH_2), 1.87 (br, 4H, $(CH_2)_2$), 1.42 (br, 9H, CH_3). FT-IR (KBr, 25 °C, cm^{-1}): 2995 (ν_{C-H}), 1732 ($\nu_{C=O}$), 1608 ($\nu_{C=N}$).

DFT Calculations:[6] Ground state density functional theory (DFT) calculations were performed using the Gaussian 16 program. Geometry optimizations of 4-Pd(II), **2**, and 4-poly-$\mathbf{1}_5$ were performed in the gas phase employing the hybrid functional B3LYP along with the 6-31G(d,p) basis set for all lighter atoms (C, H, N and O) and the LANL2DZ basis set with pseudopotential for the palladium atom. Frequency analysis was performed using the same level of theory as the optimization to confirm absence of imaginary frequencies.

Experimental procedures for iodine capture:

Iodine capture in solution:[7] In order to monitor the iodine capture of C-poly-$\mathbf{1}_m$s in solution, a time-dependent UV-Vis measurement was carried out. C-poly-$\mathbf{1}_m$s (2 mg) was added to an iodine aqueous solution (1.18 mM, 8 mL). For the iodine uptake in *n*-hexane solution, C-poly-$\mathbf{1}_m$s (2.0 mg) was added to the iodine/*n*-hexane solution (3.94 mM, 4 mL). After the addition of the polymer, the mixtures were shake by hands to facilitate the iodine capturing. The process was followed by measuring UV-Vis absortion spectra of the solution.

General procedure for iodine capture in vapor:[8] An open small vial (5 mL) containing the polymer sample (10.0 mg) was placed in a large vial (30 mL) containing iodine (500 mg). The large vial was sealed and kept in an oven at 80 °C. After a certain period, the large vial was cooled to room temperature. The small vial containing the polymers sample was weighted and placed back into the iodine-containing large vial. The large vial was sealed and put back in the oven at 80 °C to continue the adsorption till the mass of the small vial containing the polymers sample did not change.

Procedure for iodine release: In a typical experiment, I_2@C-poly-$\mathbf{1}_5$ (2.0 mg) was dispersed into methanol (40 mL) in a reaction vial with stirring. The released iodine was determined by measuring UV-Vis adsorption of the methanol solution at appropriate time intervals.

General procedure for recycling C-poly-1_5 in iodine vapor adsorption:[9] The iodine-captured I_2@C-poly-$\mathbf{1}_5$ sample was added to methanol (40 mL) in a vial at 25 °C, and the methanol was refreshed every 2 h until no color of the solution was observed. The C-poly-$\mathbf{1}_5$ sample was collected by filtration. After completely washed by methanol, it was dried under vacuum at 80 °C overnight and then reused in the iodine capture for the next cycle.

Measuring iodine adsorption capacity in solutions.[10,11] The C-poly-$\mathbf{1}_5$ (2.0 mg) powder was soaked in KI-I_2(I-3) aqueous solution (8.0 mL) of different concentrations (0.4, 0.6, 0.8, 1.0, 1.4, 1.8 mmol/L). The mixture was stirred overnight. After separation by centrifugation (10000 rpm, 10 min), the solution was detected by UV-vis spectrum.

The C-poly-$\mathbf{1}_5$ (2.0 mg) powder was soaked in 4.0 mL iodine/*n*-hexane solution of different concentration (0.2, 0.5, 1.0, 2.0, 3.9, 7.9 mmol/L). The mixture was stirred overnight. After separation by centrifugation (10000 rpm, 10 min), the solution was detected by UV-vis spectrum.

The iodine removal efficiency was measured by the following equation:

$$\text{iodine removal efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100$$

Where C_0 (mmol/L) and C_t (mmol/L) are the initial and residual concentration (after adsorption) of iodine in the stock solution and filtrate, respectively.

Kinetic adsorption studies were performed in 20 mL screw-top bottle equipped with magnetic stir bars at ambient temperature with constant stirring rate of 500 r.p.m. Firstly, C-poly-$\mathbf{1}_{\mathrm{m}}$s (2 mg) was added to an iodine aqueous solution (1.18 mM, 8 mL). The kinetic adsorption study was measured from the measurement of removal efficiency at different time interval. At any time t, if q_t is the amount of iodine adsorbed per gm of C-poly-$\mathbf{1}_{\mathrm{m}}$s adsorbent then.

$$q_t = \frac{(C_0 - C_t)M_w}{m}$$

Where m is the mass (g) of sorbent (C-poly-$\mathbf{1}_{\mathrm{m}}$s) used in this study and M_{w} is the molar mass (g/mol) of the iodine. The rate of adsorption of iodine was calculated following the Ho and McKay's pseudo-second-order adsorption model. The equation can be represented as:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_{obs} q_e^2}$$

Where q_e is the amount of iodine adsorbed (mg/g) at equilibrium time and k_{obs} is the pseudo second order rate constant (g/(mg min)) of iodine adsorption.

In order to get the maximum uptake capacity of iodine at equilibrium ($q_{max,}$) of the C-poly-$\mathbf{1}_5$ Langmuir model was followed as:

$$\frac{1}{q_e} = \frac{1}{q_{max,e}} + \frac{1}{q_{max,e} K C}$$

where q_e (mg/g) is the amount of iodine adsorbed at equilibrium time, $q_{max,e}$ (mg/g) is the maximum adsorption capacity of C-poly-$\mathbf{1}_5$ at equilibrium, K (mol^{-1}) is the equilibrium constant and c (mol/L) is the residual iodine concentration at equilibrium.

Table S1. Characterization Data for 4-poly-$\mathbf{1}_m$s[a]

run	polymers	$M_n{}^b$ (kDa)	$M_w/M_n{}^b$	Yield[c]	$\theta_{364}(\times10^3)^d$	$[\alpha]^{25}_{D}{}^e$
1	4-poly-$\mathbf{1}_{20}$	14.1	1.18	90%	–6.77	–121
3	4-poly-$\mathbf{1}_{50}$	22.3	1.20	90%	–9.71	–175
5	4-poly-$\mathbf{1}_{80}$	31.3	1.21	95%	–11.83	–193
7	4-poly-$\mathbf{1}_{100}$	38.5	1.19	83%	–13.22	–203
9	4-poly-$\mathbf{1}_{150}$	58.3	1.22	88%	–14.98	–218
11	4-poly-$\mathbf{1}_{200}$	73.5	1.20	83%	–15.03	–221

[a] The polymers were synthesized according to Scheme 1 in the main text. [b] The M_n and M_w/M_n were determined by SEC with equivalent to polystyrene standards. [c] Isolated yields. [d] The CD intensity at 364 nm of 4-poly-$\mathbf{1}_m$s measured in THF at 25 °C. [e] The optical rotations of 4-poly-$\mathbf{1}_m$s measured in THF.

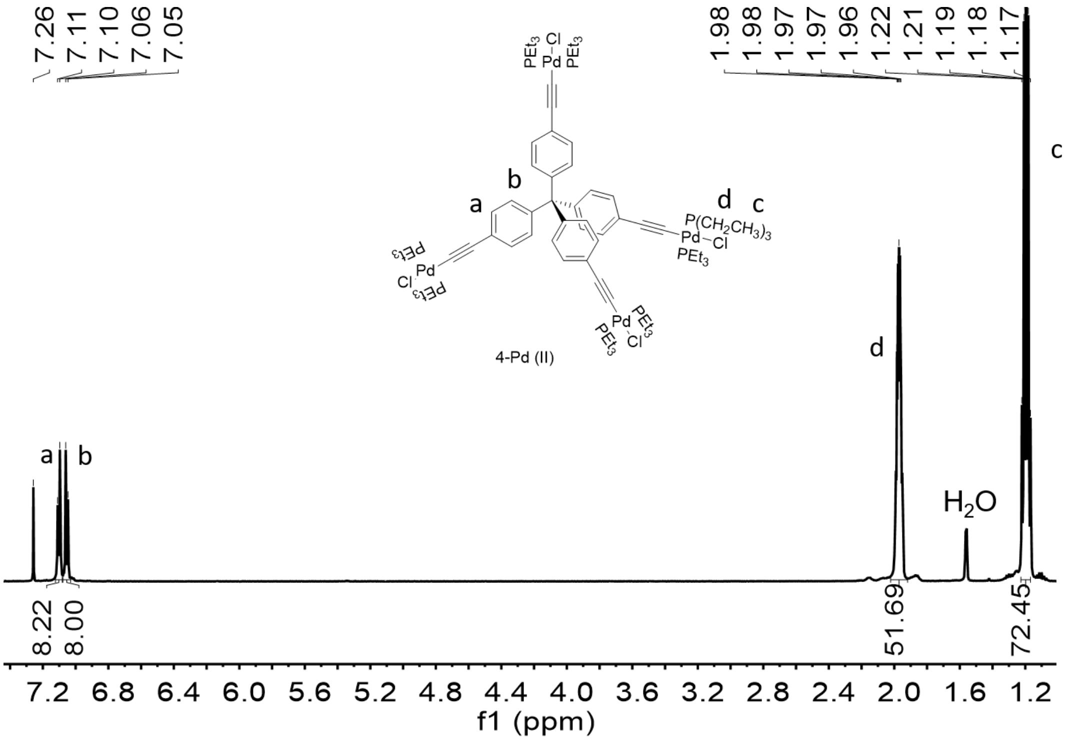


Figure S1. ^{1}H NMR (600 MHz) spectrum of 4-Pd(II) measured in $CDCl_3$ at 25 °C.

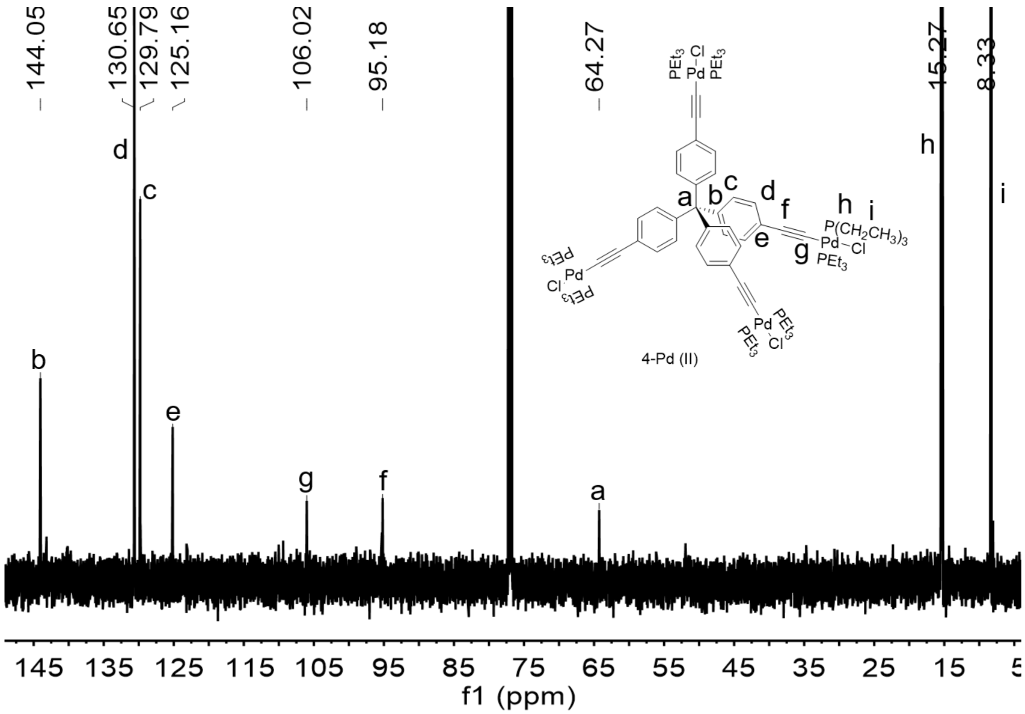


Figure S2. ^{13}C NMR (150 MHz) spectrum of 4-Pd(II) measured in $CDCl_3$ at 25 °C.

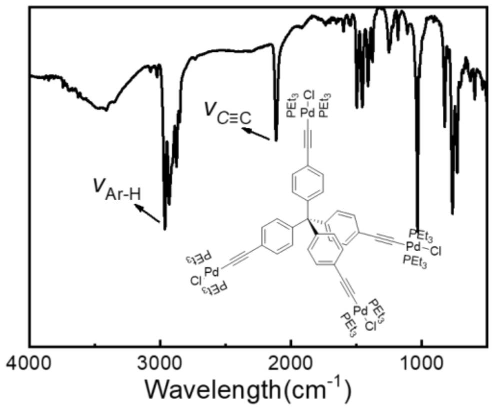


Figure S3. FT-IR spectrum of 4-Pd(II) measured at 25 °C using KBr pellets.

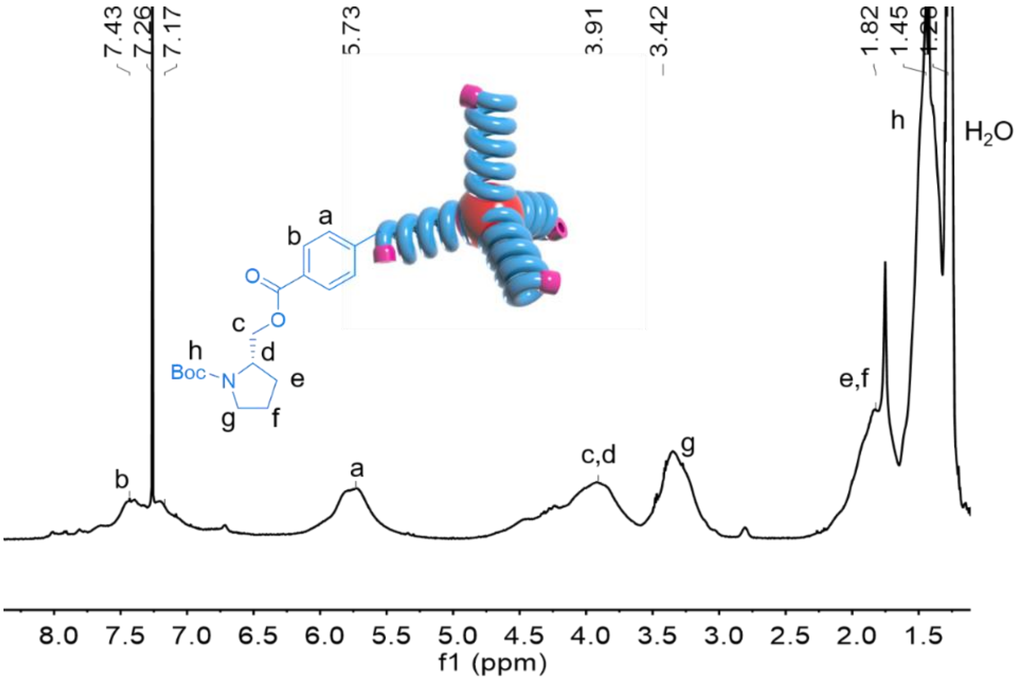


Figure S4. ^{1}H NMR (600 MHz) spectrum of 4-poly-$\mathbf{1}_{20}$ measured in $CDCl_3$ at 25 °C.

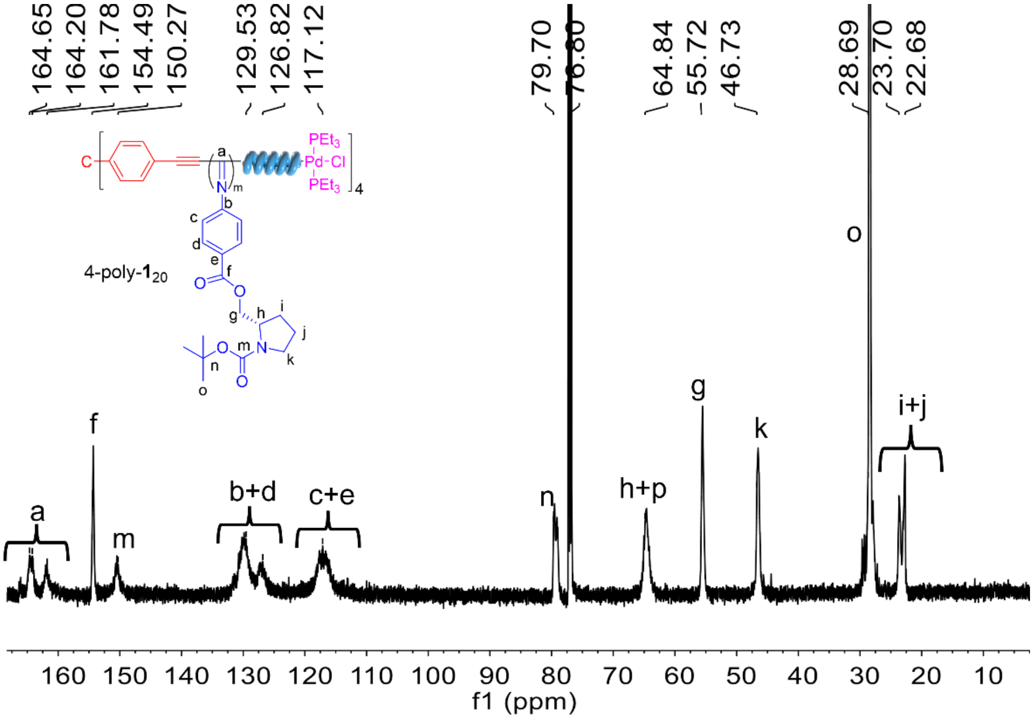


Figure S5. ^{13}C NMR (600 MHz) spectrum of 4-poly-$\mathbf{1}_{20}$ measured in $CDCl_3$ at 25 °C.

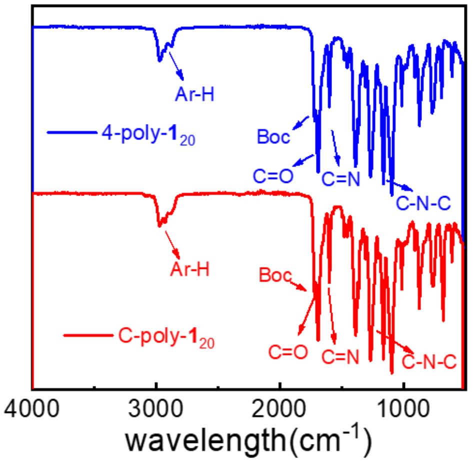


Figure S6. FT-IR spectrum of 4-poly-$\mathbf{1}_{20}$ and C-poly-$\mathbf{1}_{20}$ measured at 25 °C using KBr pellets.

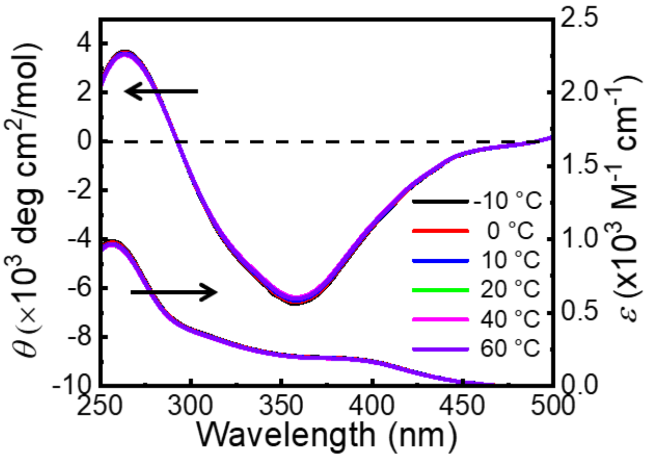


Figure S7. Temperature-dependent CD and UV-vis spectrum of 4-poly-$\mathbf{1}_{20}$ recorded in THF in a sealed cuvette.

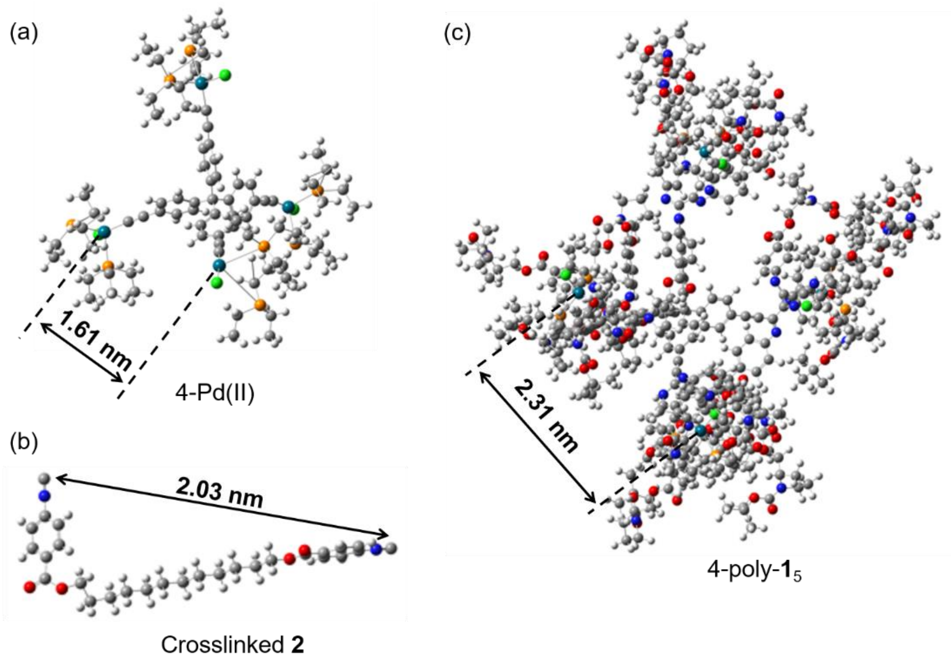


Figure S8. Geometry optimized structure of 4-Pd(II) (a), **2** (b), and 4-poly-**1**$_5$ (c) using B3LYP/LANL2DZ/6-31G(d,p) level theory.

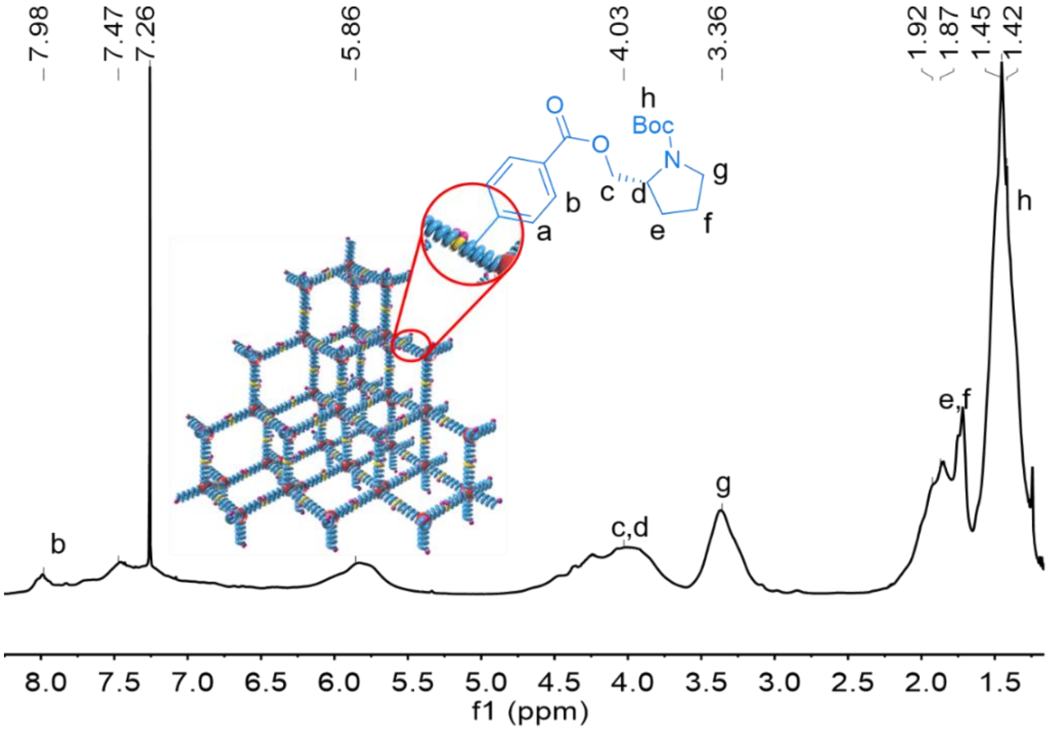


Figure S9. ^{1}H NMR (600 MHz) spectrum of C-poly-**1**$_{20}$ measured in $CDCl_3$ at 25 °C.

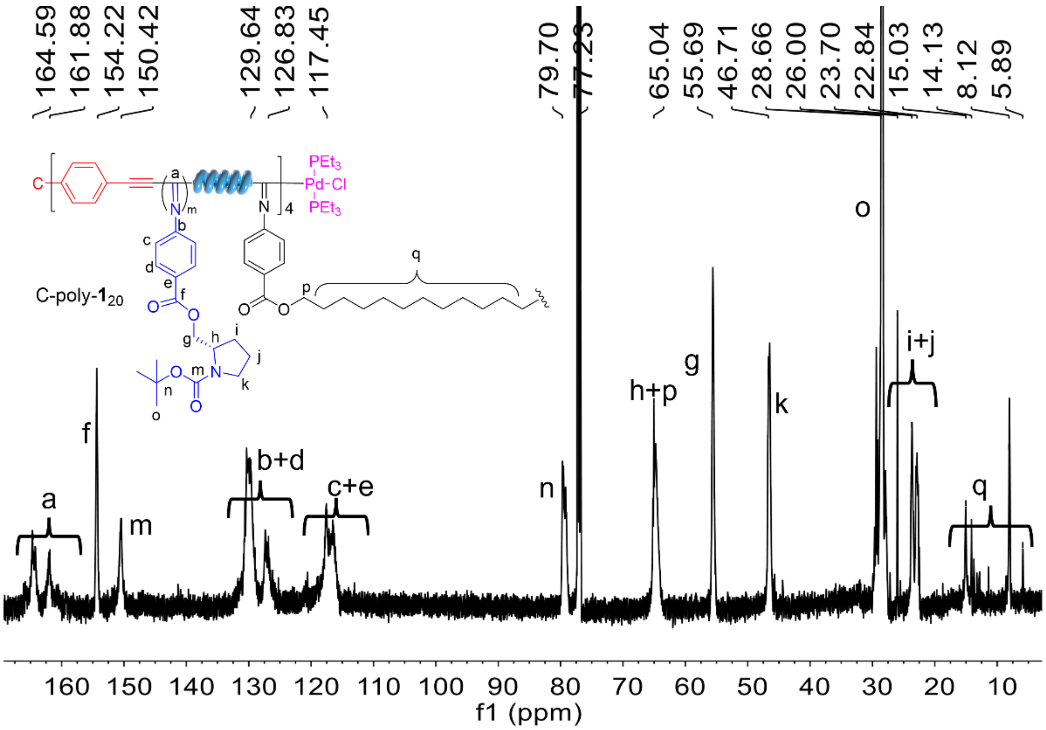


Figure S10. ^{31}C NMR (150 MHz) spectrum of C-poly-**1**$_{20}$ measured in CDCl$_3$ at 25 °C.

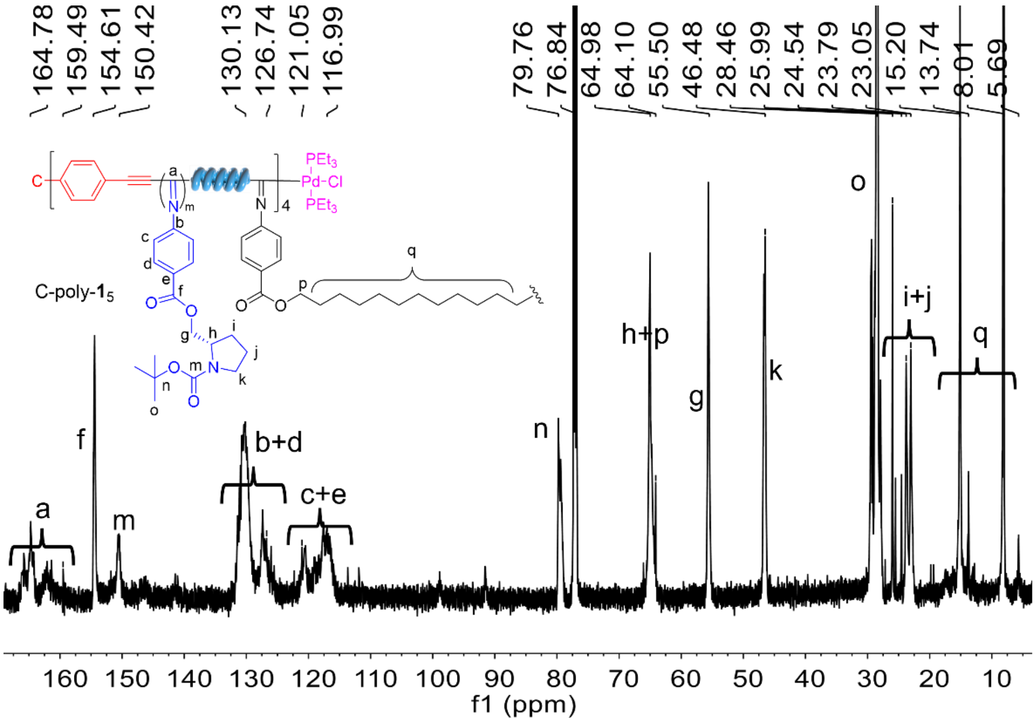


Figure S11. ^{31}C NMR (150 MHz) spectrum of C-poly-**1**$_5$ measured in CDCl$_3$ at 25 °C.

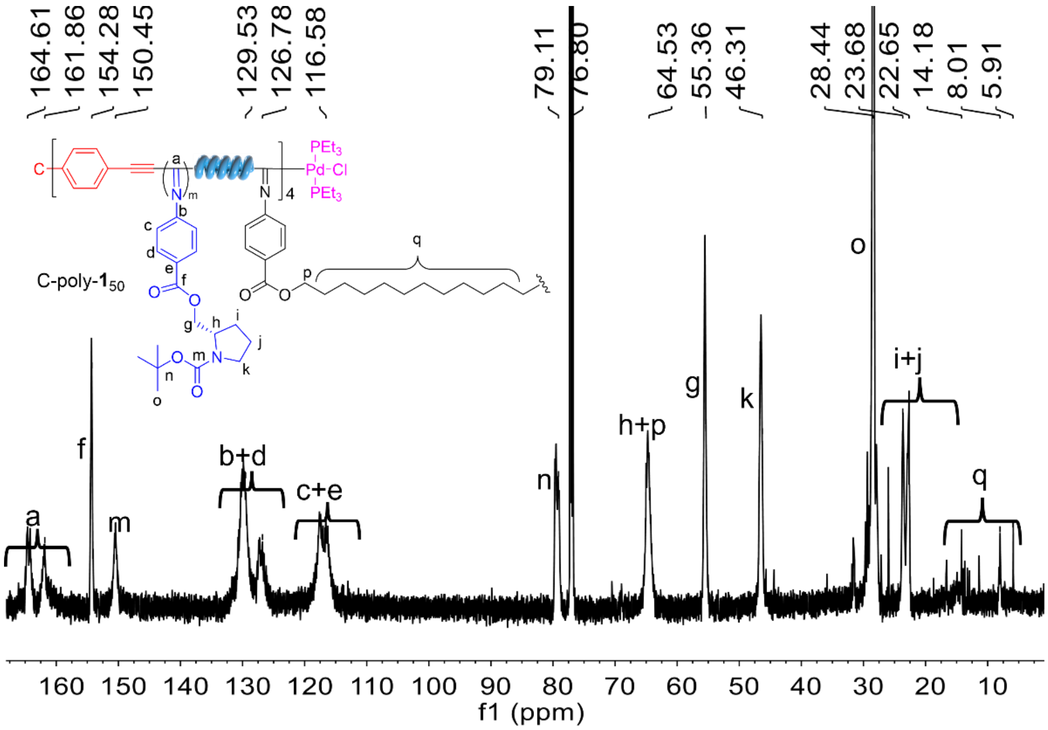


Figure S12. ^{31}C NMR (150 MHz) spectrum of C-poly-**1**$_{50}$ measured in CDCl$_3$ at 25 °C.

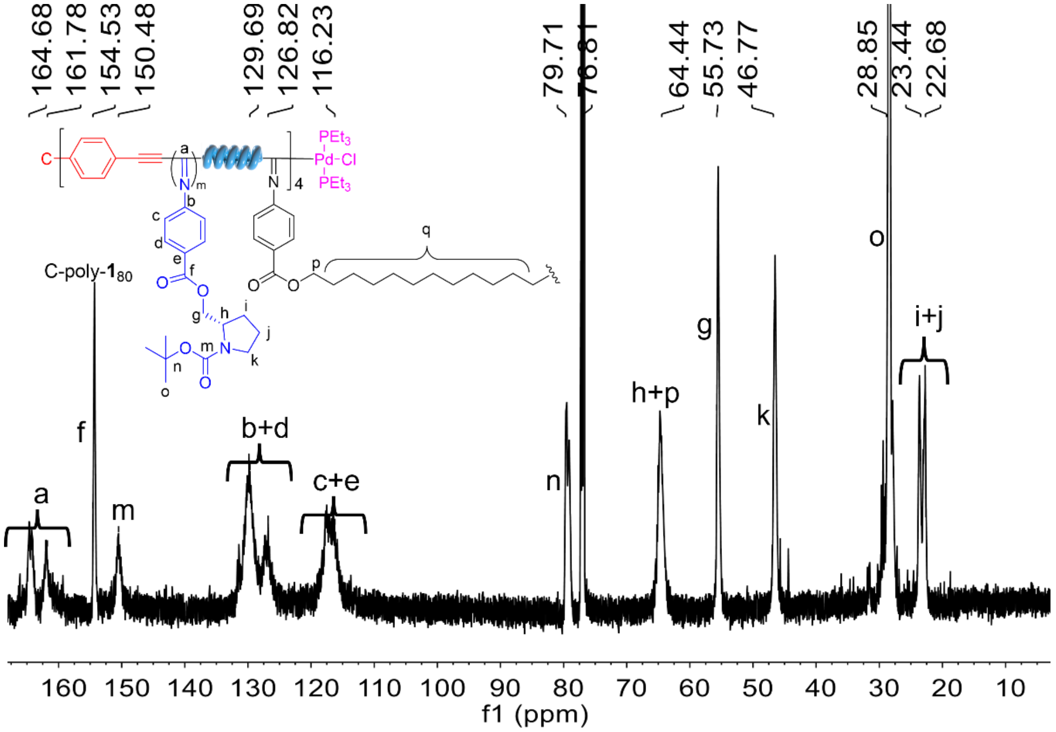


Figure S13. ^{31}C NMR (150 MHz) spectrum of C-poly-**1**$_{80}$ measured in CDCl$_3$ at 25 °C.

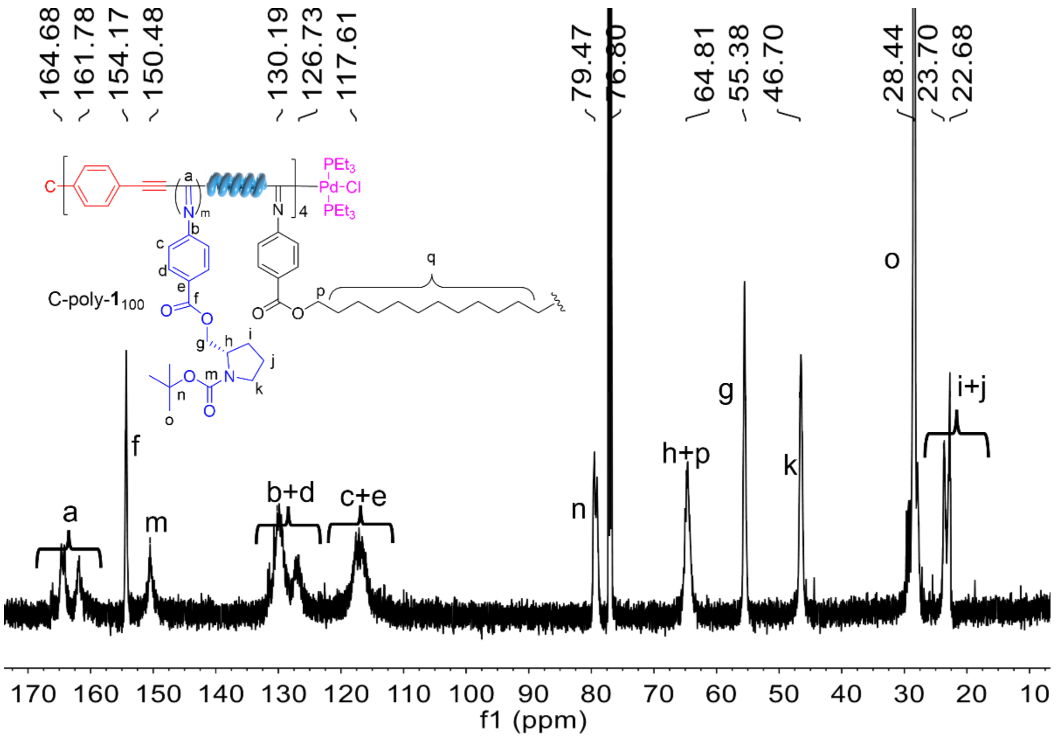


Figure S14. ^{31}C NMR (150 MHz) spectrum of C-poly-**1**$_{100}$ measured in $CDCl_3$ at 25 °C.

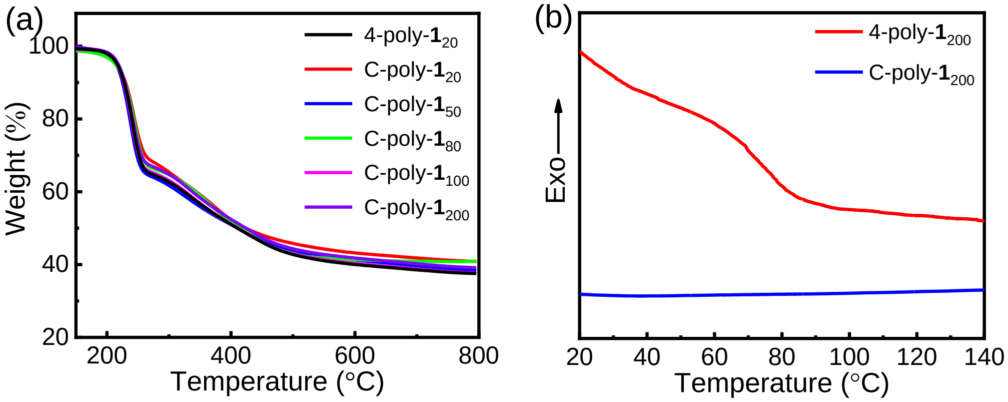


Figure S15. (a) TGA curves of 4-poly-**1**$_{20}$ and C-poly-**1**$_{m}$s with different degrees of the polymerization (DP) of the polyisocyanide segment. (b) DSC curves of 4-poly-**1**$_{200}$ and C-poly-**1**$_{200}$.

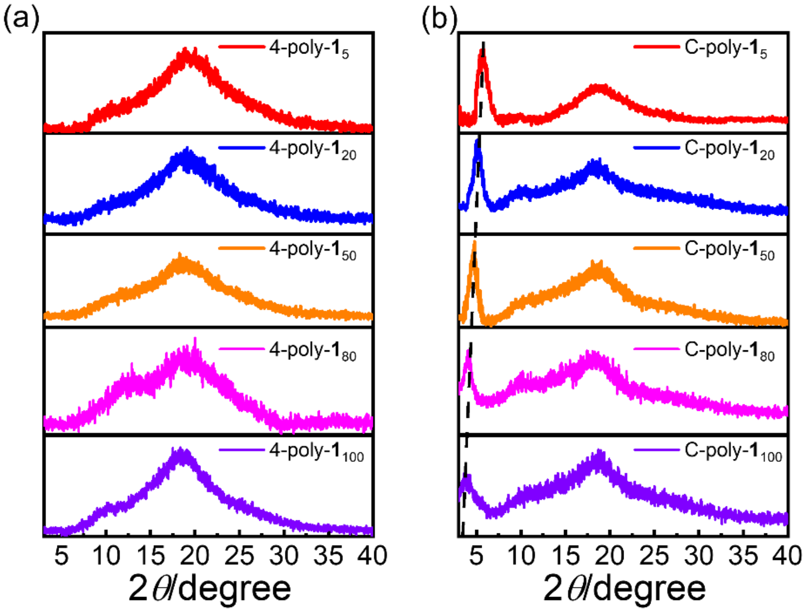


Figure S16. (a) PXRD profiles of 4-poly-$\mathbf{1}_{\mathrm{m}}$ precursors (a) and the crosslinked C-poly-$\mathbf{1}_{\mathrm{m}}$ polymers (b) with different lengths of polyisocyanide blocks.

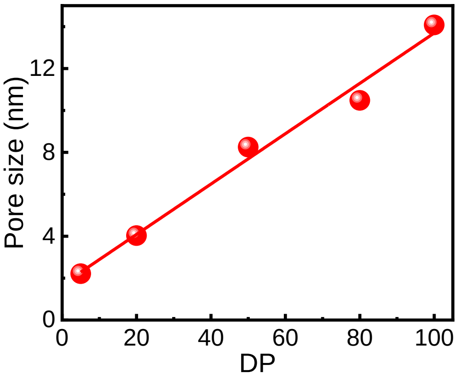


Figure S17. Plots of pore size of C-poly-$\mathbf{1}_{\mathrm{m}}$s as a function of the degree of the polymerization (DP) of the polyisocyanide blocks.

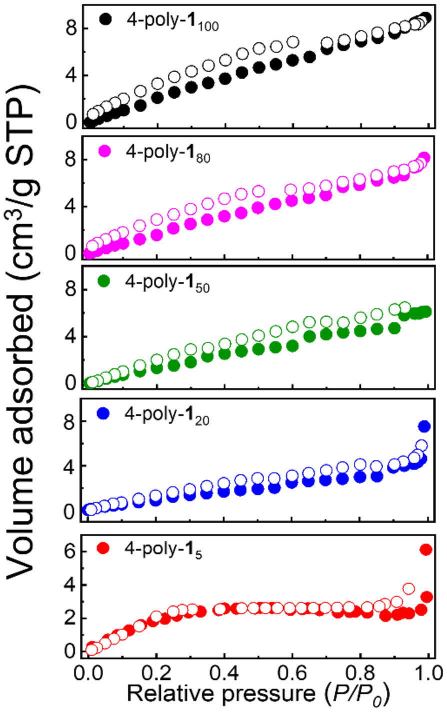


Figure S18. Nitrogen sorption isotherms of 4-poly-$\mathbf{1}_{m}$s recorded at 77 K.

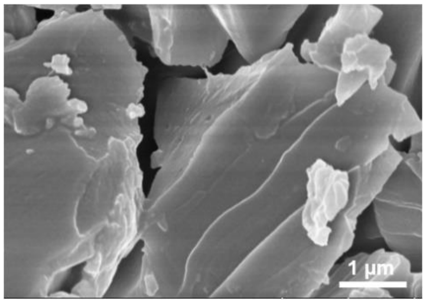


Figure S19. SEM image of the four-arm polymer 4-poly-$\mathbf{1}_{5}$.

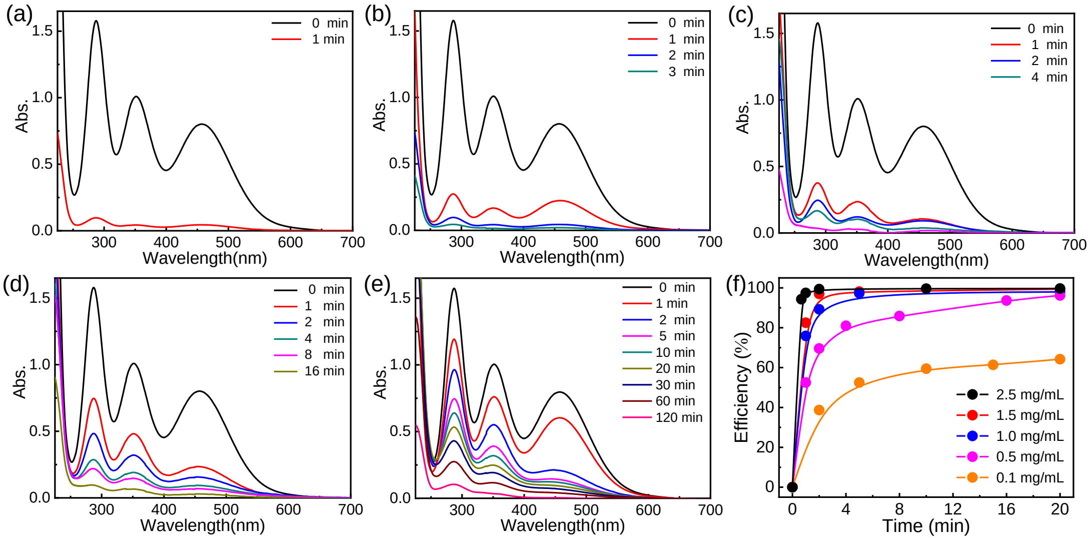


Figure S20. Time-dependent UV-vis absorption spectra of the saturated iodine aqueous solution (1.18 mM, 8 mL) upon addition of C-poly-**1**$_5$ with different amounts: (a) 20 mg, (b) 12 mg, (c) 8 mg, (d) 4 mg, and (e) 0.8 mg. (f) Plot of the adsorption efficient as a function of the amount of the polymer added in the solutions.

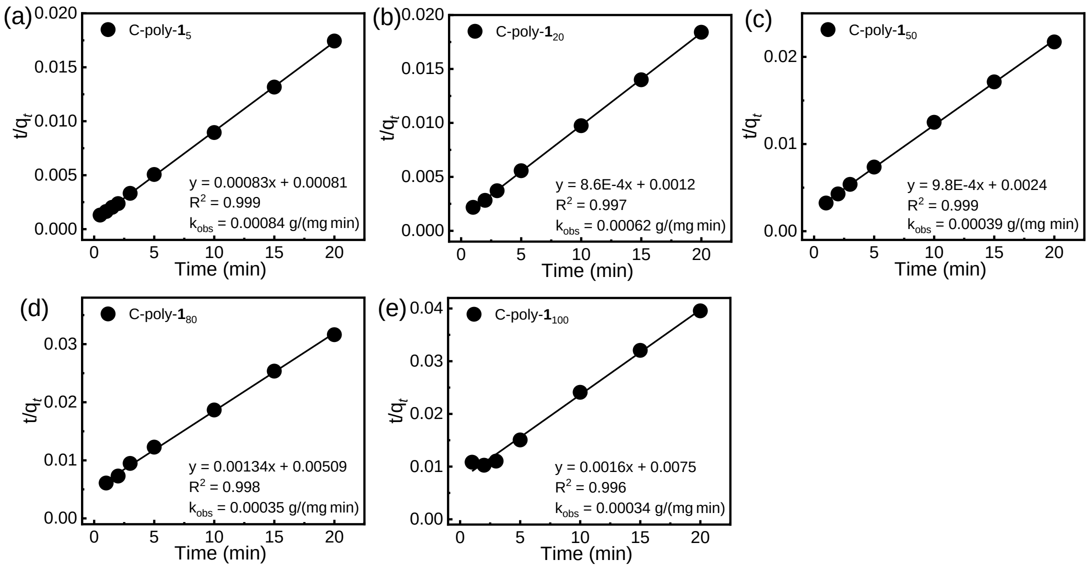


Figure S21. Plots of pseudo-second-order kinetics of C-poly-**1**$_m$s for the iodine adsorption in saturated iodine aqueous solution.

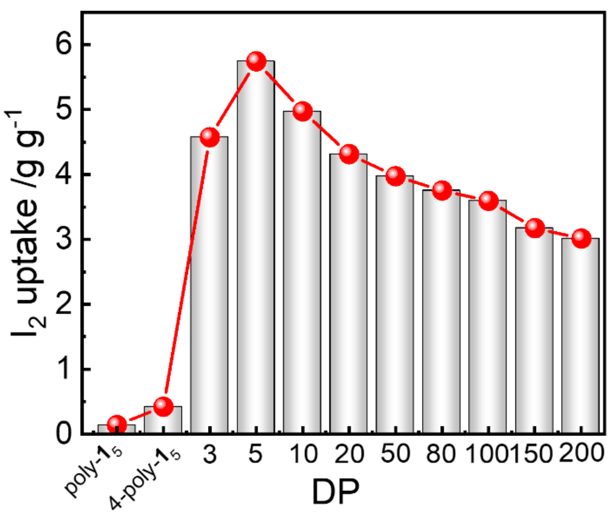


Figure S22. Plots of the iodine capture capacity of poly-$\mathbf{1}_5$, 4-poly-$\mathbf{1}_5$, and C-poly-$\mathbf{1}_m$s as a function of the degree of the polymerization (DP) of the polyisocyanide block.

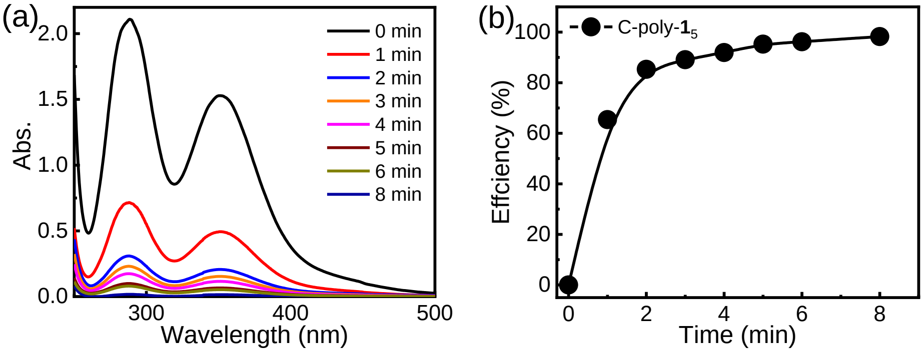


Figure S23. (a) Time-dependent UV−vis absorption spectra of the aqueous KI-I_2 solutions (0.2 mmol/L, 8 mL) with the presence of C-poly-$\mathbf{1}_5$ (2.3 mg). (b) Calculated iodine capture efficiency of C-poly-$\mathbf{1}_5$ at different times.

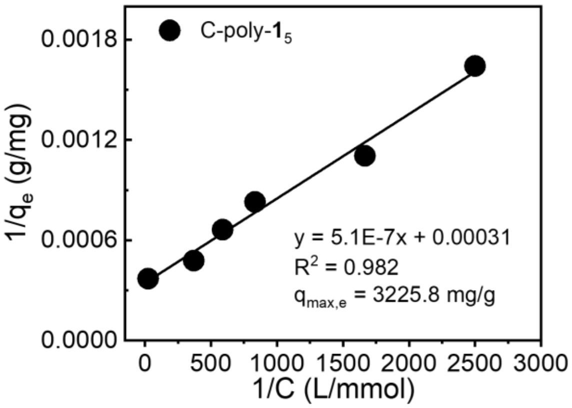


Figure S24. Langmuir model for iodine adsorption on C-poly-**1**$_5$ in aqueous KI-I_2 solution at room temperature.

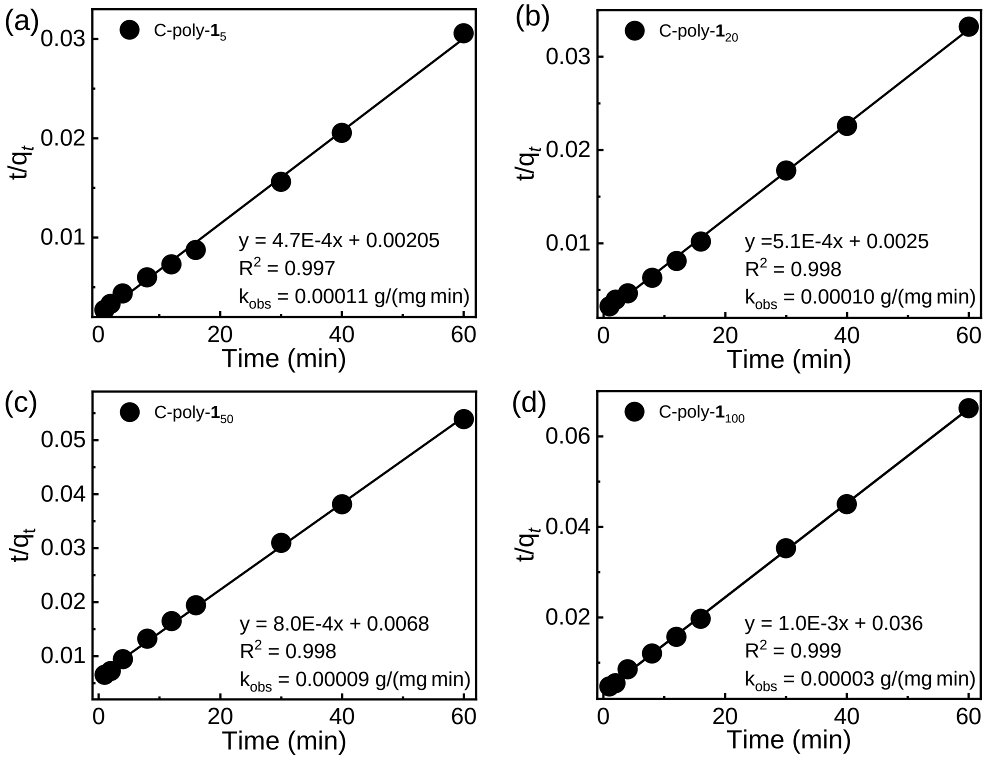


Figure S25. Plots of pseudo-second-order kinetics of C-poly-**1**$_m$s for iodine adsorption in iodine/*n*-hexane at room temperature.

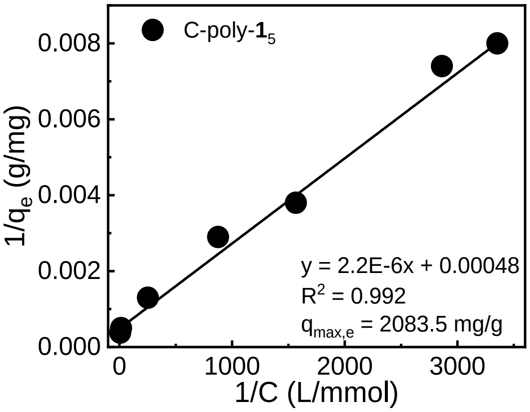


Figure S26. Langmuir model for iodine adsorption on C-poly-**1**$_5$ in iodine/*n*-hexane.

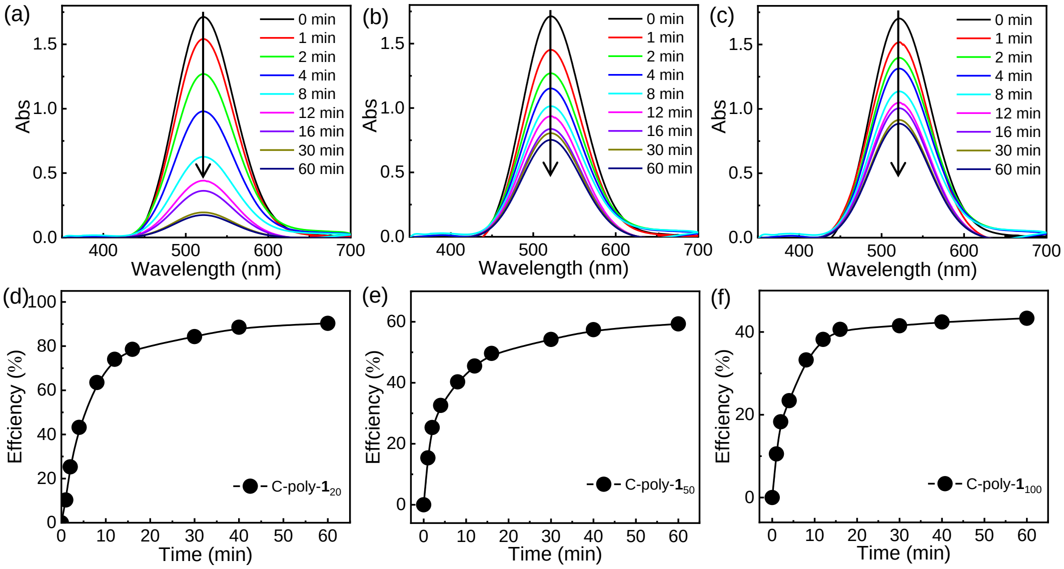


Figure S27. (a-c) Time-dependent UV-vis absorption spectra and (d-f) iodine absorption efficiency of C-poly-**1**$_{20}$ (a, d), C-poly-**1**$_{50}$ (b, e) and C-poly-**1**$_{100}$ (c, f) in iodine/*n*-hexane (3.94 mM, 4 mL) at room temperature. The polymer loading was 2.0 mg for each experiment.

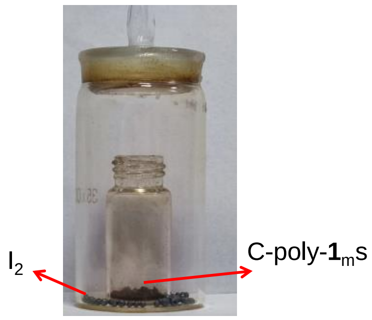


Figure S28. Device for capturing iodine in vapor by C-poly-**1**$_m$s polymers.

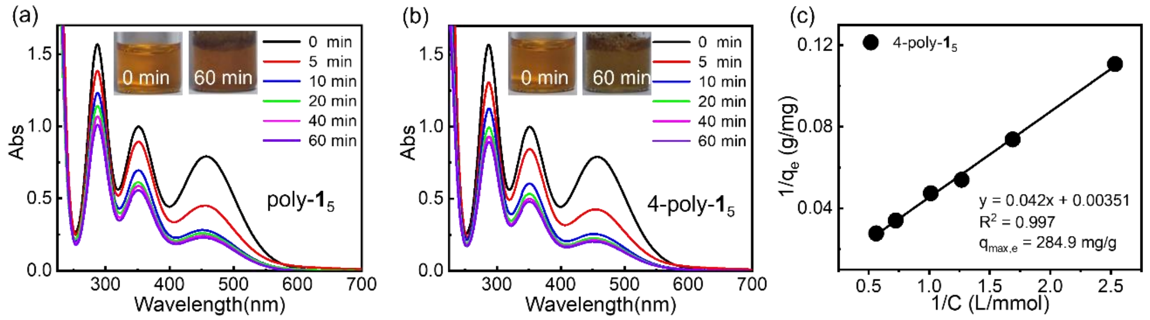


Figure S29. Time-dependent UV–vis spectra of a saturated aqueous iodine solution (1.18 mM) with the presence of poly-**1**$_5$ (a) and 4-poly-**1**$_5$ (b). (c) Langmuir model for iodine adsorption on 4-poly-**1**$_5$ in aqueous KI-I$_2$ solution at room temperature. The polymer loading was 2.5 mg/mL.

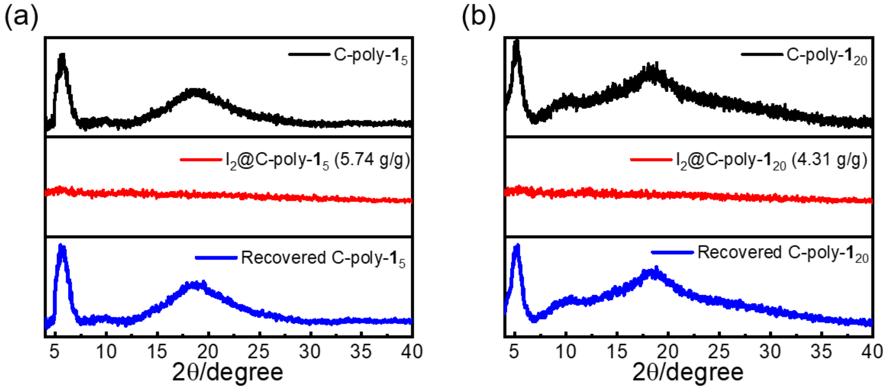


Figure S30. PXRD profiles of C-poly-**1**$_5$ (a) and C-poly-**1**$_{20}$ (b) before and after iodine adsorption.

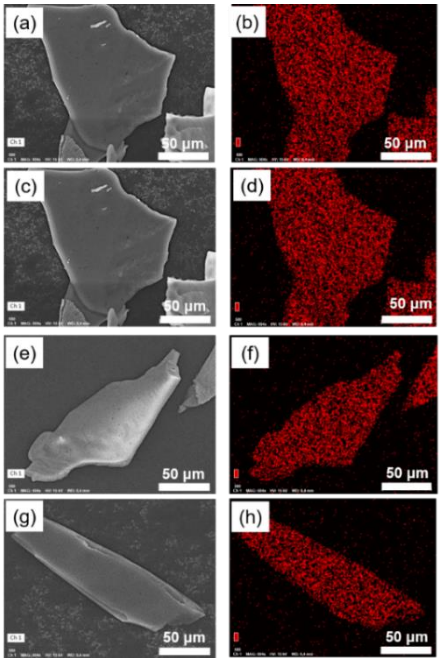


Figure S31. SEM images of I_2@C-poly-$\mathbf{1}_5$ (a), I_2@C-poly-$\mathbf{1}_{20}$ (c), I_2@C-poly-$\mathbf{1}_{50}$ (e) and I_2@C-poly-$\mathbf{1}_{100}$ (g). EDS maps of I_2@C-poly-$\mathbf{1}_5$ (b), I_2@C-poly-$\mathbf{1}_{20}$ (d), I_2@C-poly-$\mathbf{1}_{50}$ (f) and I_2@C-poly-$\mathbf{1}_{100}$ (h).

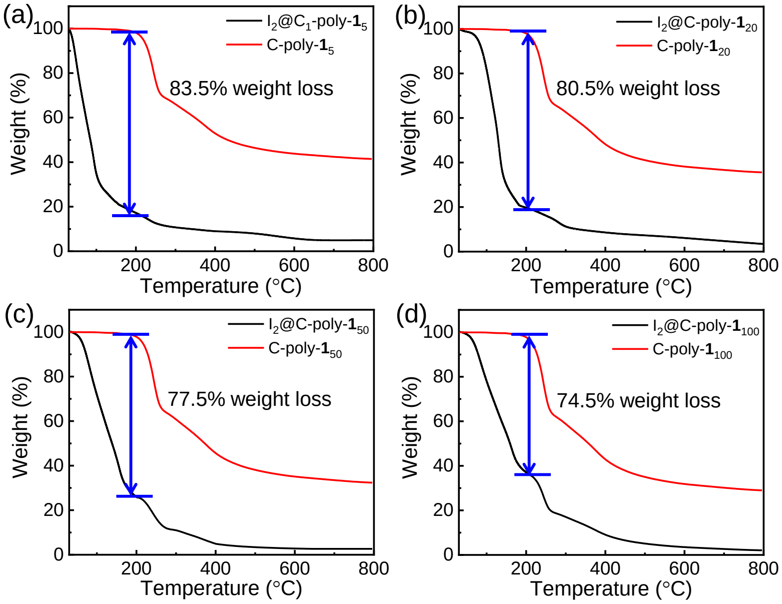


Figure S32. TGA curves of iodine-captured polymers: I_2@C-poly-$\mathbf{1}_5$ (a), I_2@C-poly-$\mathbf{1}_{20}$ (b), I_2@C-poly-$\mathbf{1}_{50}$ (c), and I_2@C-poly-$\mathbf{1}_{100}$ (d).

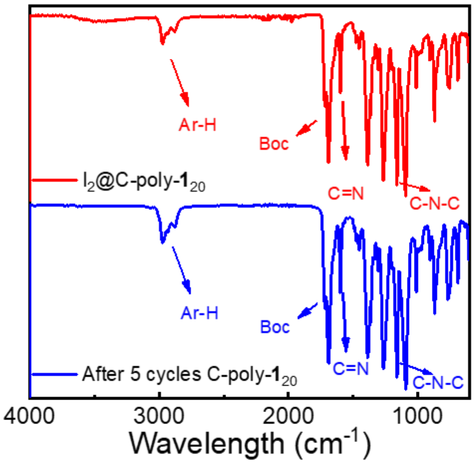


Figure S33. FT-IR spectrum of I_2@C-poly-**1**$_{20}$ and C-poly-**1**$_{20}$ after 5 cycles measured at room temperature using KBr pellets.

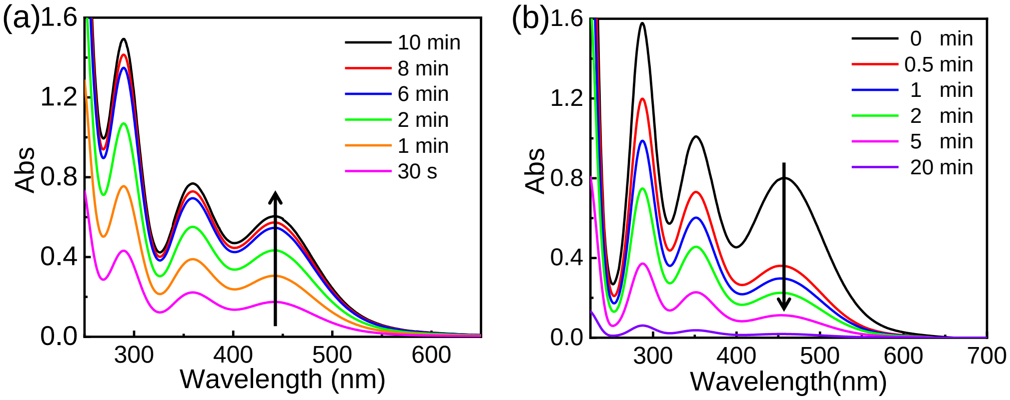


Figure 34. (a) Time-dependent UV–vis spectra of the methanol solution with the presence of I_2@C-poly-**1**$_5$. (b) Time-dependent UV–vis spectra of a saturated aqueous iodine solution (1.18 mM) in the presence of recovered C-poly-**1**$_5$.

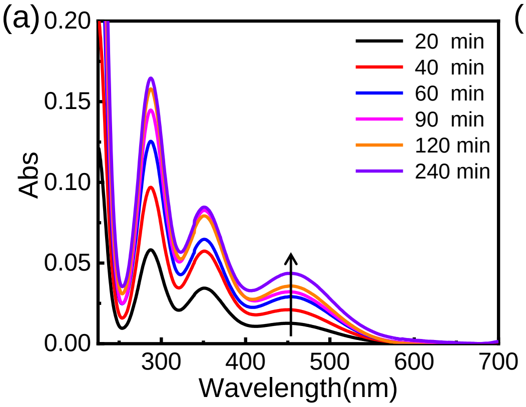


Figure 35. (a) Time-dependent UV–vis spectra of the water in the presence of I_2@C-poly-$\mathbf{1}_5$. (b) Changes over time of the absorbance at 290 and 358 nm associated with iodine release from I_2@C-poly-$\mathbf{1}_5$ into the water. I_2@C-poly-$\mathbf{1}_5$ (2.0 mg) was dispersed into water (40 mL) in room temperature.

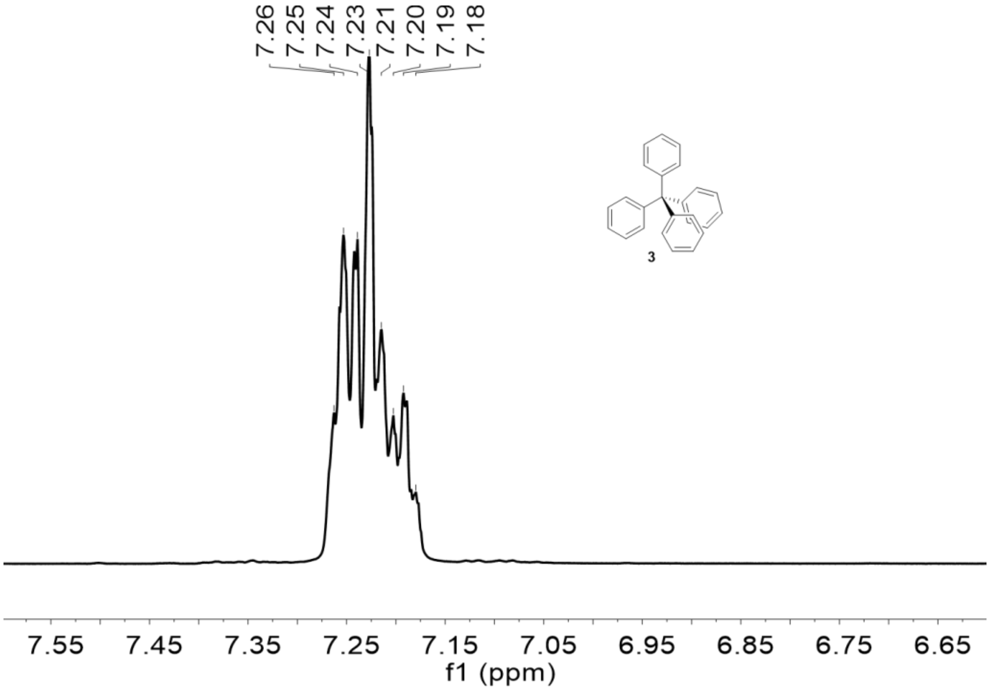


Figure S36. ^{1}H NMR (600 MHz) spectrum of **3** measured in $CDCl_3$ at 25 °C.

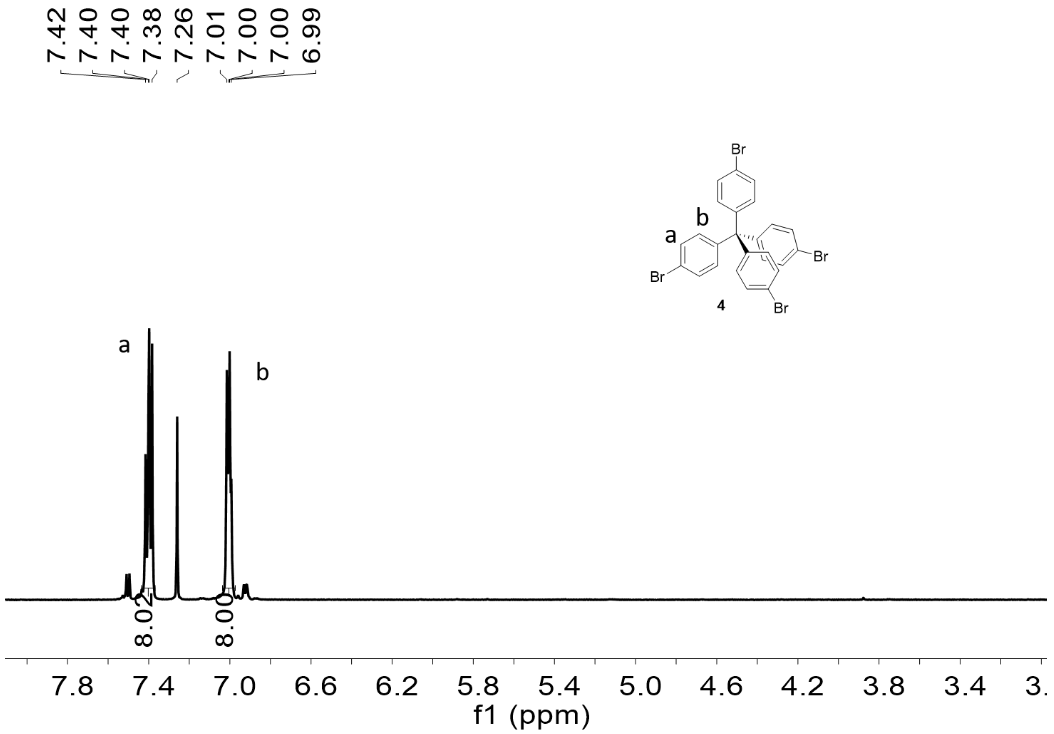


Figure S37. ^{1}H NMR (600 MHz) spectrum of **4** measured in CDCl$_3$ at 25 °C.

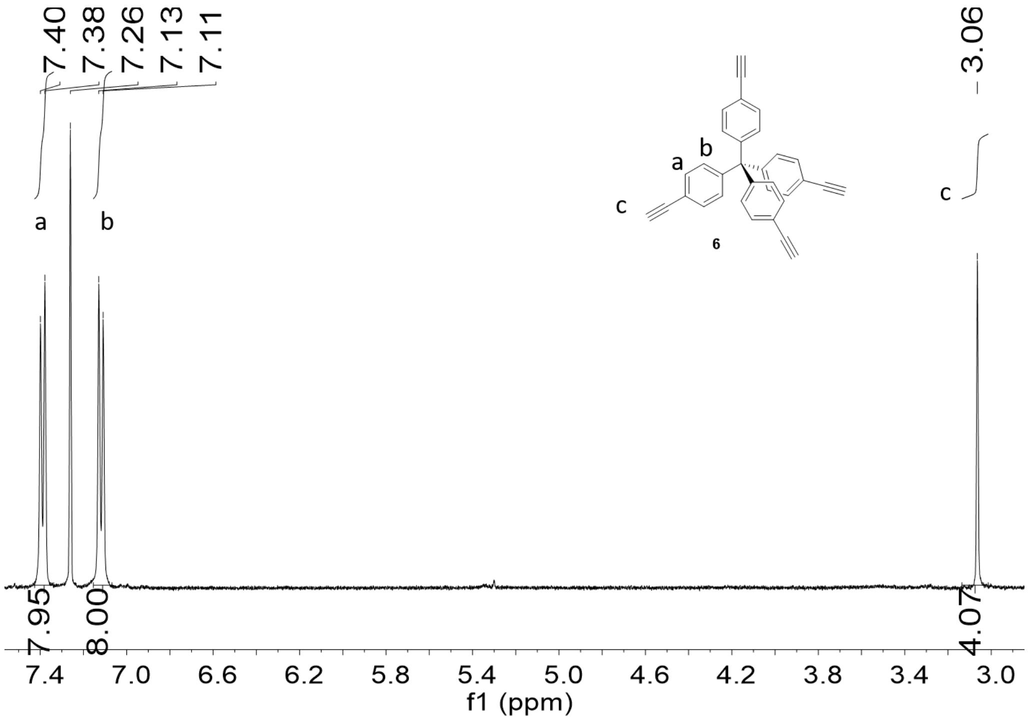


Figure S38. ^{1}H NMR (600 MHz) spectrum of **6** measured in CDCl$_3$ at 25 °C.

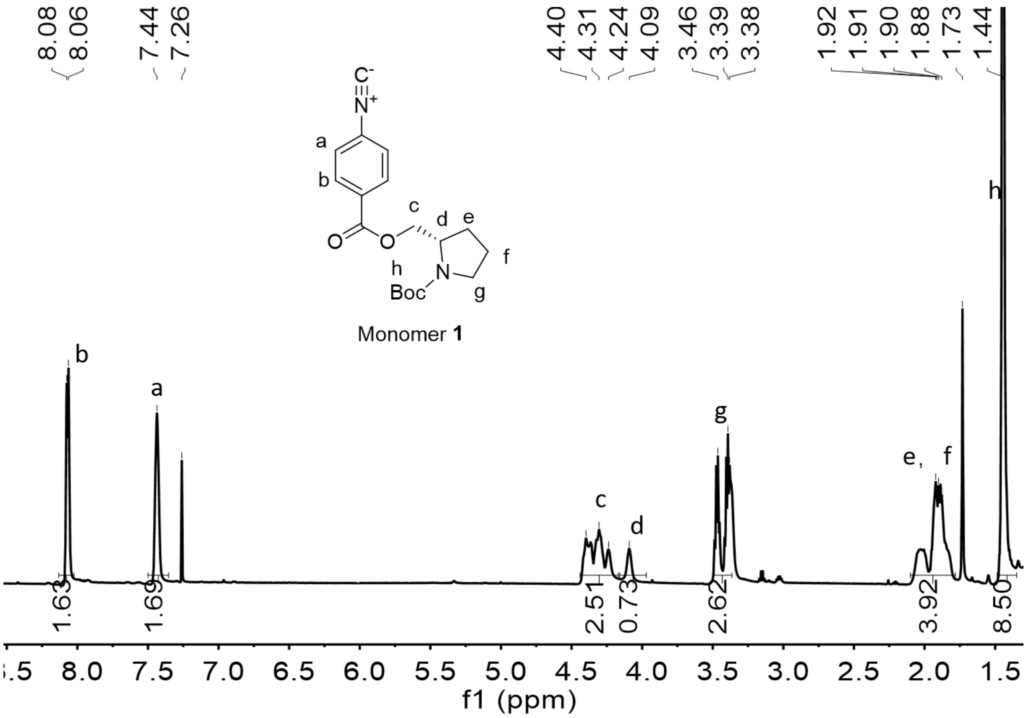


Figure S39. ^{1}H NMR (600 MHz) spectrum of monomer **1** measured in $CDCl_3$ at 25 °C.

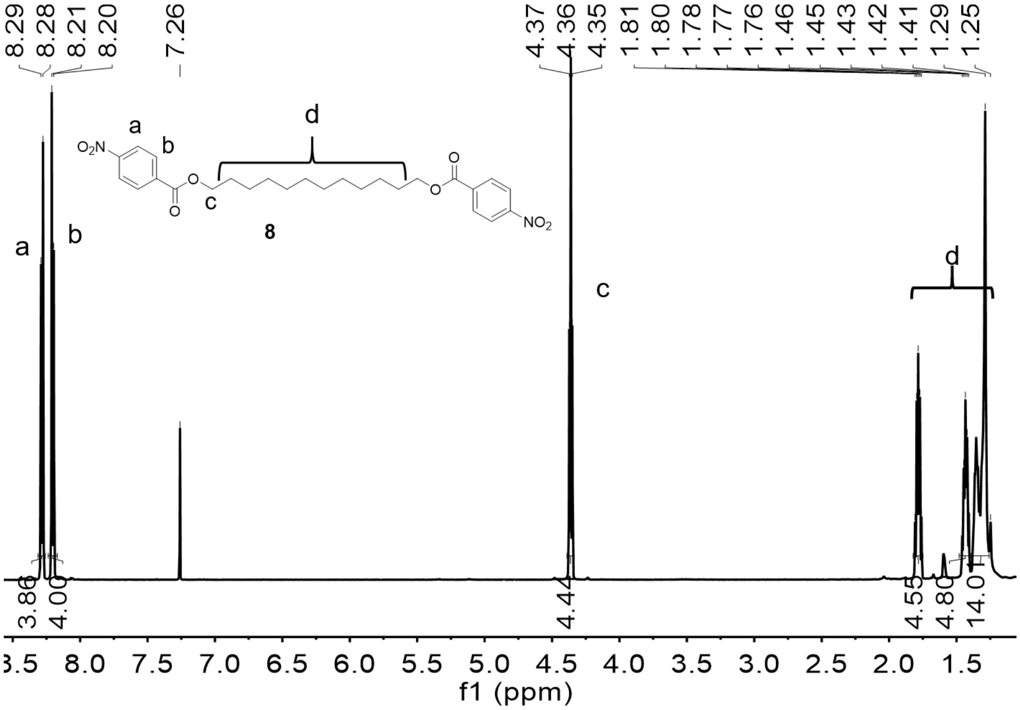


Figure S40. ^{1}H NMR (600 MHz) spectrum of **8** measured in $CDCl_3$ at 25 °C.

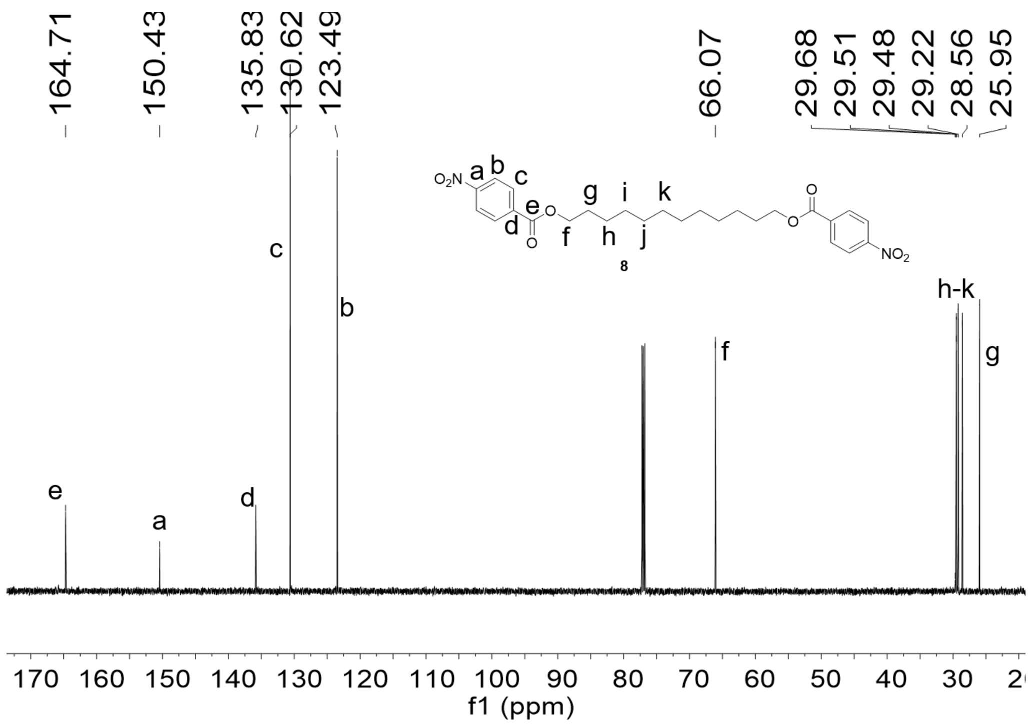


Figure S41. ^{13}C NMR (150 MHz) spectrum of **8** measured in $CDCl_3$ at 25 °C.

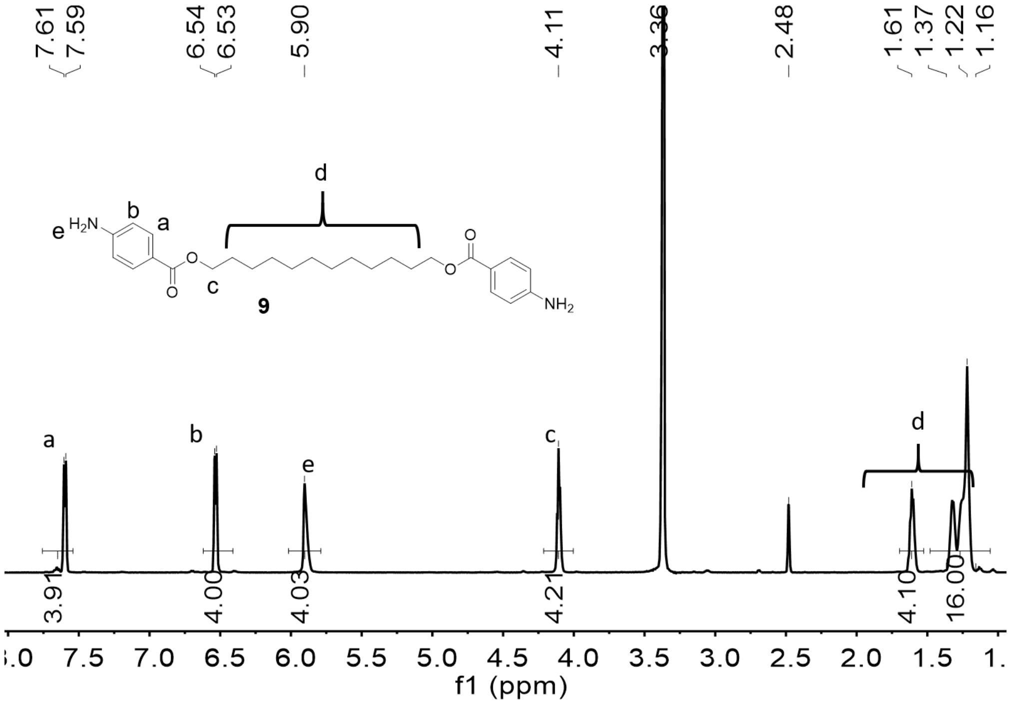


Figure S42. ^{1}H NMR (600 MHz) spectrum of **9** measured in DMSO-d_6 at 25 °C.

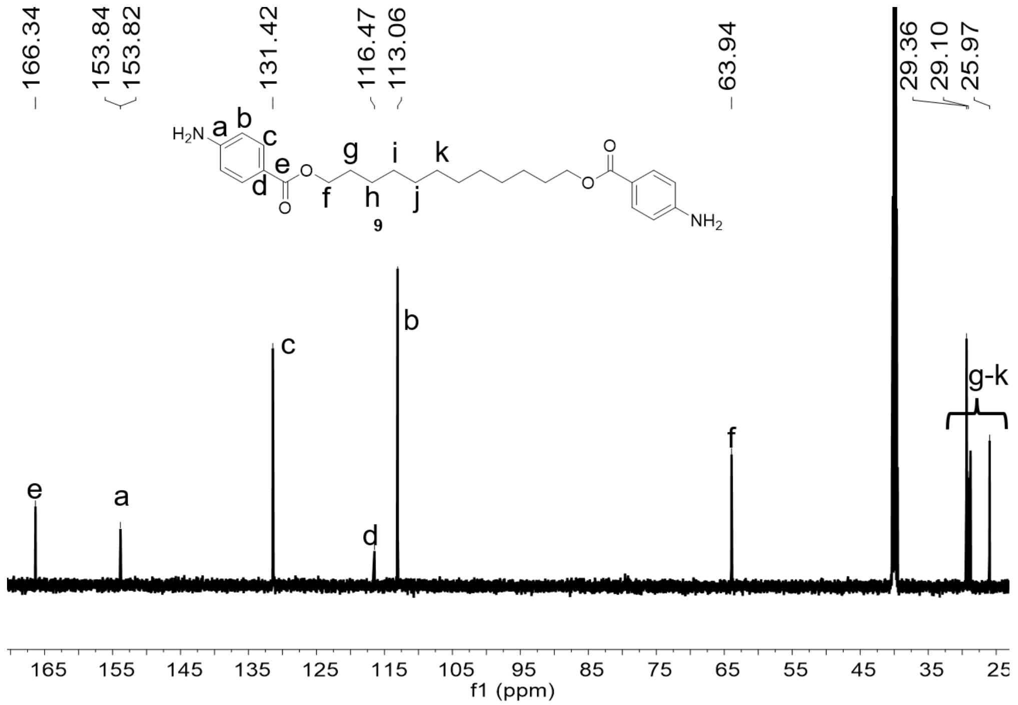


Figure S43. ^{13}C NMR (150 MHz) spectrum of **9** measured in DMSO-d_6 at 25 °C.

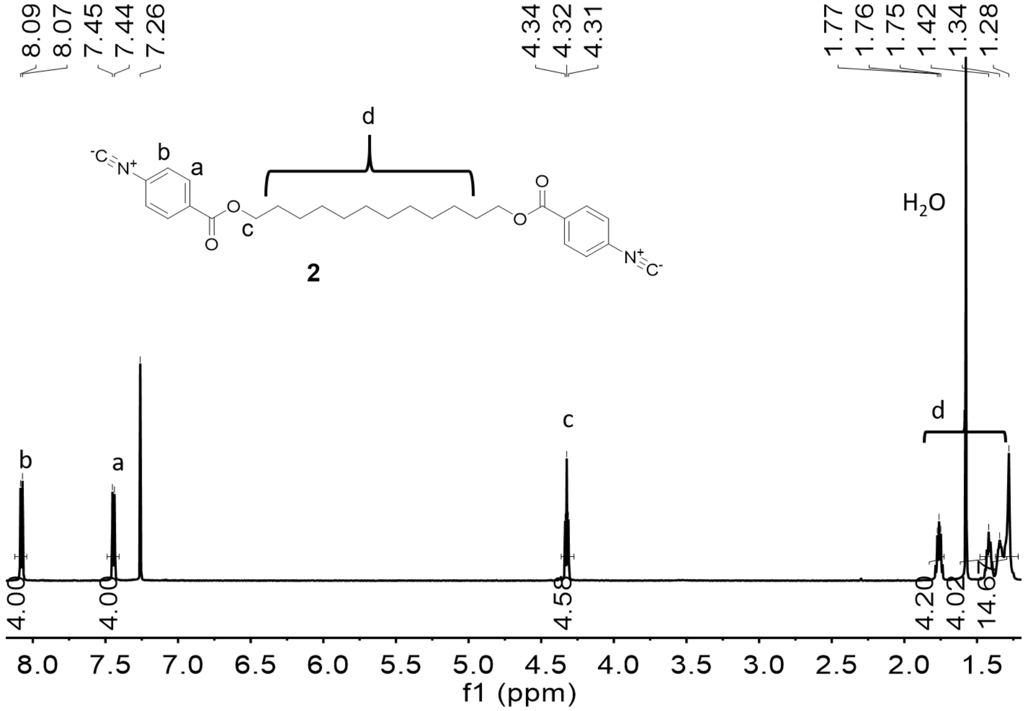


Figure S44. ^{1}H NMR (600 MHz) spectrum of cross-linker **2** measured in CDCl$_3$ at 25 °C.

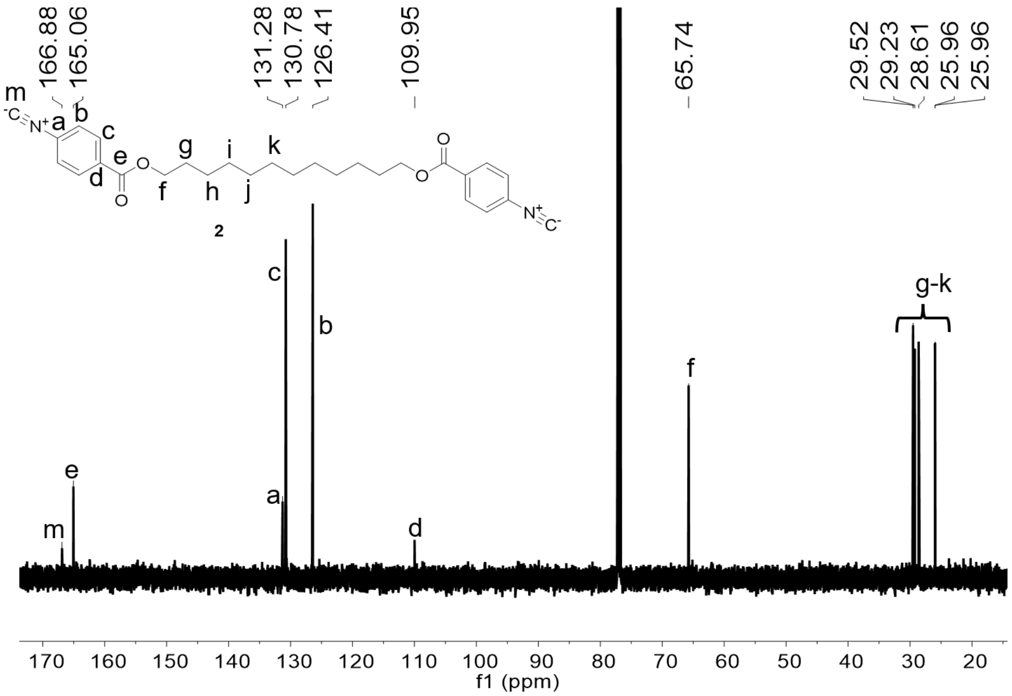


Figure S45. ^{13}C NMR (150 MHz) spectrum of **2** measured in $CDCl_3$ at room temperature.

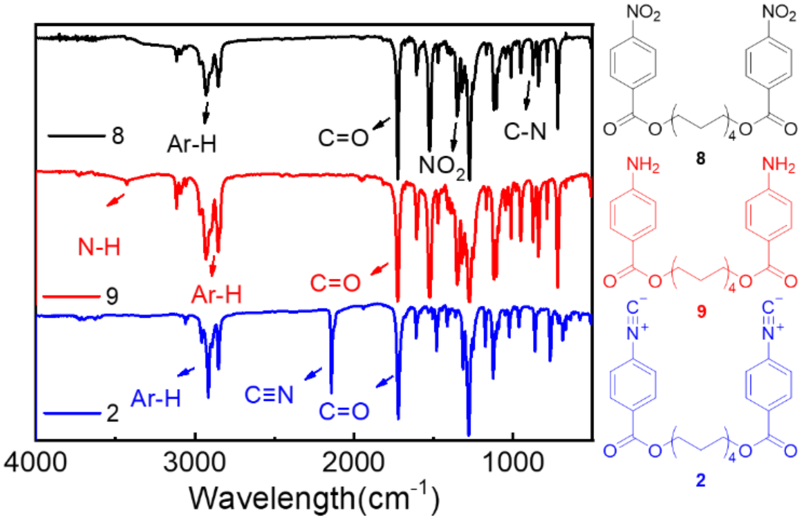


Figure S46. FT-IR spectra of **8, 9** and **2** measured at 25 °C using KBr pellets.

References

(1) Y.-X. Xue, Y.-Y. Zhu, L.-M. Gao, X.-Y. He, N. Liu, W.-Y. Zhang, J. Yin, Y. Ding, H. Zhou, Z.-Q. Wu, *J. Am. Chem. Soc*. **2014**, *136*, 4706–4713.

(2) L. Shen, L. Xu, X.-H. Hou, N. Liu, Z.-Q. Wu, *Macromolecules* **2018**, *51*, 9547– 9554.

(3) X. Zhang, X. Zhang, J. A. Johnson, Y.-S. Chen, J. Zhang, *J. Am. Chem. Soc*. **2016**, *138*, 8380–8383.

(4) J. Yin, L. Xu, X. Han, L. Zhou, C. Li, Z.-Q. Wu, *Polym. Chem*. **2017**, *8*, 545–556.

(5) J.-L. Chen, L. Yang, Q. Wang, Z.-Q. Jiang, N. Liu, J. Yin, Y. Ding, Z.-Q. Wu, *Macromolecules* **2015**, *48*, 7737–7746.

(6) U. Mandal, I. Ghiviriga, K. A. Abboud, D. W. Lester, A. S. Veige, *J. Am. Chem. Soc.* **2021**, *143*, 17276–17283.

(7) K. Jie, Y. Zhou, E. Li, Z. Li, R. Zhao, F. Huang, *J. Am. Chem. Soc.* **2017**, *139,* 15320–15323.

(8) P. Wang, Q. Xu, Z. Li, W. Jiang, Q. Jiang, D. Jiang, *Adv. Mater*. **2018**, *30*, 1801991.

(9) Y. Lin, X. Jiang, S. T. Kim, S. B. Alahakoon, X. Hou, Z. Zhang, C. M. Thompson, R. A. Smaldone, C. Ke, *J. Am. Chem. Soc*. **2017**, *139*, 7172–7175.

(10) S. Karak, K. Dey, A. Torris, A. Halder, S. Bera, F. Kanheerampockil, R. Banerjee, *J. Am. Chem. Soc*. **2019**, *141*, 7572–7581.

(11) H. Ma, J.-J. Chen, L. Tan, J.-H. Bu, Y. Zhu, B. Tan, C. Zhang, *ACS Macro Lett*. **2016**, *5*, 1039−1043.