Supporting Information:

Naturally occurring gallic acid derived multifunctional porous polymer for highly efficient CO_2 conversion and I_2 capture

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Materials: Gallic acid (98%), tannic acid (95%), 4,4'-diamonodiphenyl sulfone (99.5%), 1,3-bis(4-aminophenoxy)benzene (98%), 2-methyl-3-butyn-2-ol (98%), 3methyl-1-pentyn-3-ol (98%), 3,5-dimethyl-1-hexyn-3-ol (97%), 1-ethynyl-1cyclohexanol (97%), 3-methyl-1-nonyn-3-ol (97%), 2-phenyl-3-butyn-2-ol (98%), chloroform-D (CDCl₃, 99.8%), 1,3,5-trioxane, 1,8-diazabicyclo[5.4.0]undec-7-ene 98%), nitrite (99%), cesium (DBU, sodium carbonate (99%), 1.4diazabicyclo[2.2.2]octane (DABCO, 97%), 4-dimethylaminopyridine (DMAP, 99%), 1-methyl-2-pyrrolidone (NMP, 99%) and propylene oxide (99.5%) were provided by J&K Scientific Ltd. Silver nitrate (99.85%) and iodine (99.5%) were obtained from Acros. Na₂CO₃, HCl and other organic solvents were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. Epibromohydrin (97%) and glycidyl phenyl ether (99%) were obtained from TCI. Isobutylene oxide (98%) was purchased from Aladdin. 1,2-Epoxybutane (98%) was provided by Adamas-beta.

Characterization: The scanning electron microscopy (SEM) measurements were performed on a Hitachi S-4800 scanning electron microscope operated at 15 kV. The transmission electron microscopy (TEM) images were obtained using a TEM JEOL-1011 with an accelerating voltage of 120 kV. Powder X-ray diffraction (XRD)

patterns were collected on a Rigaku D/max-2500 X-ray diffractometer using Cu Ka radiation ($\lambda = 0.154$ nm). Fourier transform infrared (FT-IR) spectra were recorded using a Bruker Tensor 27 spectrometer and the samples were prepared by the KBr pellet method. The N₂ adsorption-desorption isotherm was determined using the Micromeritics ASAP 2020 msystem. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a ESCAL Lab 220i-XL specrometer. The content of Ag in the Ag/GA-azo-POP was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES VISTA-MPX). The content of C, H and N was obtained from elemental analysis by using the FLASH EA1112 analyzer. The thermal properties of the materials were evaluated using a thermogravimetric analysis (TGA) instrument (PerkinElmer TGA 4000) over the temperature range of 30 °C to 800 °C under N₂ atmosphere with a heating rate of 20 °C/min. NMR spectra were recorded on a Bruker Avance III HD 400 MHz NMR spectrometer. UV-Visable spectroscopy was analyzed on the UV-2600.



Scheme S1. The structural diversity of polyphenols in plants.



Fig. S1. FT-IR spectra of gallic acid, GA-azo-POP and BAPB.



Fig. S2. Solid state UV-vis spectrum of GA-azo-POP.



Fig. S3. The TEM image of GA-azo-POP.



Fig. S4. Images for the solubility of GA-azo-POP in different solvents after 10 days.



Fig. S5. Thermogravimetric analysis (TGA) profile of GA-azo-POP under N_2 atmosphere.



Fig. S6. TEM (A, B, C) and SEM (a, b, c) image of azo-POP formed from gallic acid and 4,4'-diamonodiphenyl sulfone (A, a), tannic acid and 1,3-bis(4-aminophenoxy)benzene (B, b), and tannic acid with 4,4'-diamonodiphenyl sulfone (C, c)



Scheme S2. Reaction mechanism for the carboxylative cyclization of CO_2 with propargyl alcohols over Ag/GA-azo-POP.



Fig. S7. Effect of reaction time on the cyclization of 2-methyl-3-butyn-2-ol with CO₂ or removing Ag/GA-azo-POP after 2 h (red line). Reaction conditions: 2-methyl-3-butyn-2-ol,1 mmol; Ag/GA-azo-POP, 20 mg; DBU, 1 mmol; THF, 2 mL; CO₂ pressure, 1 MPa; room temperature.



Fig. S8. Reusability of Ag/GA-azo-POP. Reaction conditions: 2-methyl-3-butyn-2-ol, 1 mmol; Ag/GA-azo-POP, 20 mg; DBU, 1 mmol; THF, 2 mL; CO₂ pressure, 1 MPa; r.t.; 1 h.



Fig. S9. The TEM image of Ag/GA-azo-POP after five cycles.



Fig. S10. The calibration curves for UV-vis absorption. The inset was the UV-vis absorbance of I_2 with different concentration monitored at 525 nm.



Scheme S3. Reaction mechanism for the cycloaddition of CO_2 with epoxides over I_2/GA -azo-POP.

Table S1. Summary of the iodine adsorption capacity in organic solvents.

	Material	Solvent	Capacity (mg/g)	Reference
Porous polymer	GA-azo-POP	Cyclohexane	287	This work
		2.07 mg/mL		
	Cu ₂ I ₂ (tppe)-2	Cyclohexane	270	Chem. Asian J.,
		2.54 mg/mL		2017, 12, 615
	AzoPPN	Hexane	150	ChemEur. J.,
		2 mg/mL		2016, 22, 11863
	NiP-CMP	Cyclohexane	150	Chem. Commun.,
		2 mg/ml		2014, 50, 8495
MOF	CdL2	Hexane	180	Chem. Commun.,
		5 mg/ml		2011, 47, 7185
	MIL series,	Cyclohexane	240	Chem.Commun.,
	CAU-1	2 mg/ml		2013, 49, 10320
	MIL-53-NH ₂	Cyclohexane	125	Chem. Commun.,
		2 mg/ml		2013, 49, 10320

NMR data of the α-alkylidene cyclic carbonates



4,4-Dimethyl-5-methylene-[1,3]dioxolan-2-one:

¹H NMR (400 MHz, CDCl₃) δ =4.78 (d, *J* = 4.0 Hz, 1H), 4.34 (d, *J* = 4.0 Hz, 1H), 1.62 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ =158.74, 151.31, 85.36, 84.64, 27.60.





4-Ethyl-4-methyl-5-methylene-[1,3]dioxolan-2-one: ¹H NMR (400 MHz, CDCl₃) δ = 4.82 (d, *J* = 3.9 Hz, 1H), 4.28 (d, *J* = 3.9 Hz, 1H), 1.92 (dq, *J* = 14.7, 7.4 Hz, 1H), 1.77 (dq, *J* = 14.7, 7.4 Hz, 1H), 1.59 (s, 3H), 0.99 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ =157.29, 151.49, 87.60, 85.56, 33.26, 25.85, 7.23.





4-Isobutyl-4-methyl-5-methylene-[1, 3] dioxolan-2-one: ¹H NMR (400 MHz, CDCl₃) δ =4.80 (d, *J* = 1.8 Hz, 1H), 4.27 (s, 1H), 1.83 (dt, *J* = 18.7, 6.0 Hz, 2H), 1.71 – 1.61 (m, 1H), 1.58 (s, 3H), 1.02 – 0.95 (m, 6H); ¹³C NMR (101 MHz, CDCl₃) δ =158.40, 151.59, 87.44, 85.69, 77.44, 77.12, 76.80, 48.61, 27.11, 24.38, 24.08, 23.77.





4-Methylene-1, 3-dioxa-spiro [4.5] decan-2-one: ¹H NMR (400 MHz, CDCl₃) δ=4.76 (d, *J* = 3.9 Hz, 1H), 4.31 (d, *J* = 3.9 Hz, 1H), 2.06 – 1.97 (m, 2H), 1.85 – 1.58 (m, 7H), 1.40-1.23 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ=158.54, 151.32, 86.33, 85.40, 36.30, 24.15, 21.49.







4-Hexyl-4-methyl-5-methylene-[1,3]dioxolan-2-one: ¹H NMR (400 MHz, CDCl₃) δ =4.80 (d, *J* = 3.9 Hz, 1H), 4.27 (d, *J* = 3.9 Hz, 1H), 1.87 (ddd, *J* = 14.5, 11.0, 5.2 Hz, 1H), 1.77 – 1.64 (m, 1H), 1.58 (s, 3H), 1.46 – 1.24 (m, 9H), 0.88 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ =157.84, 151.61, 87.35, 85.53, 40.48, 31.55, 28.98, 26.37, 22.96, 22.53, 14.05.





4-Methyl-5-methylene-4-phenyl-[1,3]dioxolan-2-one: ¹H NMR (400 MHz, CDCl₃) δ =7.52 – 7.35 (m, 5H), 4.94 (d, *J* = 4.0 Hz, 1H), 4.47 (d, *J* = 4.0 Hz, 1H), 1.97 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ =157.36, 151.15, 139.23, 129.15, 128.89, 124.66, 88.20, 87.15, 27.41.



