Experimental section

Synthesis of (4-HOMe₂CC=CC₆H₄)₃N.^[1] 2-Methylbut-3-yn-2-ol (9.7 mL, 100.0 mmol) was added to a mixture of tris(p-bromophenyl)amine (4.82 g, 10.0 mmol), PdCl₂(PPh₃)₂ (0.28 g, 0.4 mmol) and CuI (152 mg, 0.8 mmol) in 100 mL of triethylamine. The reaction mixture was heated to 80 °C for 48 h. Next, the solvents were removed by rotary evaporation under reduced pressure. The residue was extracted with ethyl acetate and filtered. The filtrate was washed with water and saturated brine solution. The organic layer was dried over anhydrous magnesium sulfate, and the solvents removed by rotary evaporation under reduced pressure to give the crude product as a dark oil. The crude product was purified by a silica gel column chromatography using hexane/ethyl acetate (1:1) as eluent. After recrystallization from ethyl acetate/hexane the product was obtained as yellow crystals (4.21 g, 85.6%). ¹H NMR (600 MHz, CDCl₃) δ (TMS, ppm): 7.35-7.30 (m, 6H), 6.99 (d, 6H), 2.05 (s, 3H), 1.63 (d, 18H). ¹³C NMR (150 MHz, CDCl₃) δ (TMS, ppm): 146.71, 132.81, 123.88, 117.43, 93.64, 81.85, 65.66, 31.54. MS (APLI): calcd. 491.25; found 491.237.



Synthesis of tris(4-ethynylphenyl)amine.^[1] (4-HOMe₂CC=CC₆H₄)₃N (3.932 g, 8.0 mmol) and powdered KOH (6.732 g, 120.0 mmol) were suspended in 300 mL of toluene and stirred at 80 °C overnight. The reaction mixture was filtered through a short pad of celite after cooling down to room temperature. The celite pad was washed with toluene three times and the combined organic phases were evaporated under reduced pressure. The resulting oil was purified by a silica gel column chromatography using hexane/CH₂Cl₂ (4:1) as eluent gave tris(4-ethynylphenyl)

amine as a yellow solid (2.17 g, 85.5%). ¹H NMR (400 MHz, CDCl₃) δ (TMS, ppm):7.44 (d, 6H), 7.07 (d, 6H), 3.08 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (TMS, ppm): 147.04, 133.37, 123.93, 116.89, 83.40, 77.32 (s). GCMS (EI): calcd. 317.12; found 317.10.



Synthesis of 4-iodophenyl-substituted graphene (RGO-I). Graphene oxide (GO) was prepared from graphite flakes according to a modified Hummers method.^[2] GO (400 mg) was reduced with hydrazine hydrate (N₂H₄·H₂O) in the presence of sodium dodecylbenzenesulfonate (SDBS) under reflux.^[3] The functionalization of reduced graphene oxide (RGO) was carried out according to a published procedure (Scheme S1).^[4-7] The 4-iodophenyl diazonium salt that is used for the functionalization of graphene was prepared *in situ* starting from 4-iodoaniline: 4-iodoaniline (1.535 g, 7 mmol) were dissolved in 80 ml of deionized water by adding conc. aqueous HCl dropwise in a round bottom flask. The 4-iodoaniline solution was then kept at 0 °C in an ice bath. To this solution, NaNO₂ (526 mg, 7.6 mmol) was added and stirred for 45 min. The colour of the solution changed from colorless to yellow with the formation of the diazonium salt.

The solution of the diazonium salt was next added dropwise to the RGO dispersion under rapid stirring. The reaction mixture was maintained at 0 °C for additional 2 hours. After stirring at room temperature for additional 4 hours, the mixture was poured into acetone. The product RGO-I was purified by filtration and washing with deionized water, acetone, and N,N-dimethylformamide (DMF). The solid product was dried in vacuum at room temperature (yield: 376 mg RGO-I).



Scheme S1. Idealized formula scheme depicting the reduction of GO and functionalization of the resulting RGO with 4-iodophenyl side groups under formation of RGO-I.

Synthesis of graphene-based conjugated microporous polymers (GMPs). The GMPs were synthesized by palladium-catalyzed Sonogashira-Hagihara cross-coupling reactions of RGO-I^[5, 8] with tris(4-ethynylphenyl)amine and the specific aryl halide building block (2,5-dibromopyridine, or 2,5-dibromopyrazine, or 2,4,6-trichloro-1,3,5-triazine, Scheme S2). The synthesis of GMP1N as a representative experimental procedure is given below.

Synthesis of GMP1N. RGO-I (100 mg) was sonicated in dry DMF (150 mL) until complete dispersion occurs. Then, tris(4-ethynylphenyl)amine (317 mg, 1 mmol), 2,5-dibromopyridine, (235mg, 1 mmol), tetrakis-(triphenylphosphine) palladium (35 mg, 0.03 mmol), copper iodide (14 mg, 0.06 mmol), and Et_3N (20 mL) were added to the RGO-I dispersion. The reaction mixture was heated to 120 °C and stirred for 3 days under argon atmosphere. Next, the insoluble, precipitated product was filtered off and washed four times with chloroform, water, and acetone to remove unreacted

monomers or catalyst residues. Further purification of the product was carried out by Soxhlet extraction with THF for 48 h. The product was dried under vacuum for 24 h at room temperature to afford GMP1N (yield: 447 mg).



Scheme S2. Preparation of graphene-based conjugated microporous polymer sandwiches and corresponding graphene-free conjugated microporous polymers by palladium-catalyzed Sonogashira-Hagihara cross-coupling reaction.

Characterization. Solution NMR spectra were recorded on Bruker AVANCE 400 or AVANCE III 600 machines. ¹H and ¹³C NMR spectra were measured with tetramethylsilane (TMS) as internal standard. Fourier transform infrared (FTIR) spectroscopy was carried out on a JASCO FT/IR-4200 Fourier-Transform-spectrometer. UV-Vis absorption spectra were recorded on a Shimadzu UV-2401 PC spectrophotometer at room temperature. The morphology of G-CMPs and corresponding carbon nanosheets were characterized by transmission electron microscopy (TEM, JEOL, JEM-2100F). The TEM samples were prepared by transferring G-CMPs and corresponding carbon nanosheets onto copper grids. Thermogravimetric analysis were performed on a Mettler Toledo TGA Stare System

under argon flow. Raman spectra were recorded on a LabRAM HR Raman Microscope with an excitation wavelength of 514 nm. X-ray photoelectron spectroscopy (XPS) was carried out on a Kratos AXIS Ultra, performing at 15 kV and 15 mA with a monochromatic Al K α source (hv = 1486.71 eV).

Nitrogen adsorption-desorption measurements. The nitrogen adsorption-desorption measurements were performed on a BELSORB Max (BEL Japan Inc.). The surface areas were calculated using the BET model in the pressure range p/p_0 from 0.05-0.3. The total pore volume was determined at a relative pressure of 0.99. The pore size distribution was analyzed from the nitrogen adsorption data using by NLDFT analysis with a slit pore model.

Solid-state NMR measurements. The measurements have been performed on a Bruker Avance III console operating at 700 MHz 1H Larmor frequency, using a commercial 2.5 mm double resonance MAS NMR probe, spinning at 25 kHz MAS spinning frequency. The CP contact time was 2ms in order to sufficiently polarize even non-protonated 13C sites.

Supercapacitor fabrication. Coin-cell-type symmetric supercapacitors were fabricated to evaluate the supercapacitive performance. Briefly, 80 wt% porous carbon materials (GMP2NC or MP2NC), 10 wt% active carbon, and 10 wt% polyvinylidene fluoride (PVDF, as binder) were homogeneously mixed into a paste. Then, the mixture was rolled onto a nickel foil as current collector. After drying at 120 °C overnight, the electrodes/collectors were assembled into CR2032 stainless steel coin cells with 6 M aqueous KOH solution and a porous cellulose membrane as electrolyte and separator, respectively.

Electrochemical measurements and caculations. The electrochemical experiments were carried out using a conventional three-electrode system employing 6 M KOH aqueous solution as electrolyte at room temperature. The three-electrode cells consist

of Ag/AgCl as reference electrode, Pt as counter electrode, and the porous carbon materials as working electrode. The working electrode was prepared by loading our porous carbon materials onto a glassy carbon electrode. Thereby, the porous carbon materials were first dispersed in water by sonication under formation of a homogeneous dispersion (1mg/mL). Next, 5 μ L of the dispersion were loaded onto a glassy carbon electrode with a diameter of 5 mm. The modified electrode was slowly dried in air until a uniform layer was formed at the electrode surface. The following cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) measurements in both three-electrode and two-electrode arrangements were performed using a PAR VersaSTAT 4 electrochemical workstation.

The specific capacitance was calculated by the following equation:

$$C = I \Delta t / m \Delta V$$

where C (F/g) is the specific capacitance, I (mA) the discharge current, and Δt (s), m (mg), and ΔV (V) the total discharge time, the mass of active material, and the potential drop (by excluding the voltage (IR) drop) during discharge, respectively.

The energy density (E) was calculated from the discharge profiles of the twoelectrode system by using the following equation:

$$E=0.5C \Delta V^2/3.6$$

where E (Wh kg⁻¹) is the energy density, C (F g⁻¹) the specific capacitance of the active material and ΔV (V) the discharge voltage range. With a factor 3.6, the energy density is converted from J g⁻¹ to Wh kg⁻¹.

The power density (*P*) was calculated as follows:

$$P=E\times 3600/\Delta t$$

where P (kW kg⁻¹) is the power density, and E (Wh kg⁻¹) and Δt (s) energy density

and discharge time, respectively.



Figure S1. TEM image of RGO-I and photograph of RGO-I dispersion in DMF.



Figure S2. FTIR spectra of tris(4-ethynylphenyl)amine, the aryl halides (2,5-dibromopyridine, 2,5-dibromopyrazine, and 2,4,6-trichloro-1,3,5-triazine) and the corresponding graphene-based conjugated microporous polymers (GMP1N, GMP2N and GMP3N).



Figure S3. ¹³C CP/MAS NMR spectra of (a) GMP2N and (b) GMP3N.



Figure S4. XPS spectra of graphene-based, conjugated microporous polymers.



Figure S5. TEM images of (a) GMP1N and (b) GMP3N. (c) TEM and (d) HRTEM images of GMP2N.



Figure S6. SEM (left) and TEM (right) images of MP2N.



Figure S7. (a) Cumulated pore volume and (b) surface area as a function of pore width for graphene-based, conjugated microporous polymers.



Figure S8. (a) Nitrogen adsorption/desorption isotherms, (b) pore size distribution, (c) cumulated surface areas, and (d) pore volumes as function of the pore width for the graphene-free conjugated microporous polymers.



Figure S9. TGA profiles of graphene-based, conjugated microporous polymers and corresponding graphene-free, conjugated microporous polymers.



Figure S10. (a) Cumulated pore volumes, and (b) surface areas as a function of pore width for GMP-derived carbon nanosheets.



Figure S11. (a) Nitrogen adsorption/desorption isotherms, (b) pore size distributions, (c) cumulated surface areas, and (d) pore volumes as function of the pore width for the carbons derived from graphene-free conjugated microporous polymers.



Figure S12. (a) XPS spectra of GMP-derived carbon nanosheets. High resolution XPS C 1s spectra of (b) GMP1NC, (c) GMP2NC and (d) GMP3NC.



Figure S13. CV curves of (a) GMP1NC, (b) MP1NC, (c) GMP2NC, (d) MP2NC, (e) GMP3NC, and (f) MP3NC at different scan rates in a three-electrode system using 6 M aqueous KOH solution as electrolyte.



Figure S14. (a-e) CV curves for RGO, RGO-I, GMP1N, GMP2N and GMP3N, respectively, at different scan rates in a three-electrode system using 6 M aqueous KOH solution as electrolyte. (f-j) GCD curves and (k-o) gravimetric capacitances for RGO, RGO-I, GMP1N, GMP2N and GMP3N, respectively, at different charge/discharge current densities.



Figure S15. GCD curves of (a) GMP1NC, (b) MP1NC, (c) GMP2NC, (d) MP2NC, (e) GMP3NC, and (f) MP3NC at different charge/discharge current densities in a three-electrode system using 6 M aqueous KOH solution as electrolyte.



Figure S16. Gravimetric capacitances for (a) GMP1NC and MP1NC, (b) GMP2NC and MP2NC, and (c) GMP3NC and MP3NC at different charge/discharge current densities in a three-electrode system using 6 M aqueous KOH solution as electrolyte.



Figure S17. CV curves of (a) GMP2NC- and (b) MP2NC-based supercapacitors at the scan rates from 10 to 200 mV/s using 6 M aqueous KOH solution as electrolyte.



Figure S18. GCD curves of (a, b) GMP2NC- and (c, d) MP2NC-based supercapacitors at different charge/discharge current densities using 6 M aqueous KOH solution as electrolyte.



Figure S19 Area-normalized capacitances at different charge-discharge current densities of GMP2NC- and MP2NC-based supercapacitors.



Figure S20 Cycling performance in terms of capacitance retention at 5 A/g for a GMP2NC-based supercapacitor (the capacitance from the first cycle is set to 100%).

sample	$\mathbf{S}_{\mathrm{BET}}$	Smicro	S _{meso}	V _{total}	V _{micro}	V _{meso}
	(m^{2}/g)	(m^{2}/g)	(m^{2}/g)	(cm^3/g)	(cm^{3}/g)	(cm^{3}/g)
MP1N	739	722	17	0.39	0.36	0.03
MP2N	632	621	11	0.31	0.28	0.03
MP3N	699	653	46	0.4	0.33	0.07
GMP1N	842	764	78	0.44	0.31	0.13
GMP2N	852	758	94	0.50	0.31	0.19
GMP3N	816	699	117	0.47	0.29	0.18

Table S1. Summary of the N_2 sorption data for the conjugated porous polymers andgraphene-templated, conjugated porous polymers.

Table S2. Summary of the N_2 sorption data for the porous carbon materials without or with graphene templates.

sample	S _{BET}	S _{micro}	S _{meso}	V _{total}	V _{micro}	V _{meso}
	(m^2/g)	(m^{2}/g)	(m^{2}/g)	(cm^3/g)	(cm^{3}/g)	(cm ³ /g)
MP1NC	746	738	8	0.35	0.28	0.07
MP2NC	883	881	2	0.35	0.33	0.01
MP3NC	909	893	16	0.45	0.34	0.11
GMP1NC	523	483	40	0.26	0.18	0.12
GMP2NC	642	597	45	0.35	0.22	0.13
GMP3NC	693	639	54	0.36	0.24	0.12

Table S3. Comparison of the gravimetric capacitances of carbon-based supercapacitor

 electrode materials from the literature.

Materials	Gravimetric capacitance	Flectrolyte	References	
	(F/g)	Liectiolyte		
Reduced graphene oxide	41.5 (0.1 A/g)	6 M KOH	[9]	
Reduced graphite oxide with high density	182 (1 A/g)	6 M KOH	[10]	
High density porous graphene macroform	238 (0.1 A/g)	6 M KOH	[11]	
Porous graphene nanosheets	241 (2 mV s ⁻¹)	6 M KOH	[12]	
Hydrazine reduced graphene oxide	123 (10 mV s ⁻¹)	6 M KOH	[13]	
Graphene sponge	204.66 (5 mV s ⁻¹)	1 M NaCl	[14]	
Activated microways sufalisted graphite suids	137 (1 A/g)	BMIM BF ₄ /AN	[15]	
Activated interowave extended graphite oxide	154 (1 A/g)	EMIM TFSI/AN	[10]	
KOH activated graphene	166 (0.7 A/g)	BMIM BF ₄ /AN	[16]	
Compressed KOH activated graphene	147 (1.24 A/g)	BMIM BF ₄ /AN	[17]	
S-porous carbon/graphene	109 (0.05 A/g)	6 M KOH	[18]	
Activated graphene-derived carbon	174	Ionic liquid	[19]	
Nitrogen-enriched nonporous carbon	115 (0.05 A/g)	1 M H ₂ SO ₄	[20]	
Seaweeds derived carbon	198 (2 mV s ⁻¹)	1 M H ₂ SO ₄	[21]	
Activated carbon aerogel	220 (0.125 A/g)	1 M H ₂ SO ₄	[22]	
Copper nanocrystal modified activated carbon	79 (0.2 A/g)	TEATFB	[23]	
N-doped reduced graphene oxide	255 (0.5 A/g)	6 М КОН	[24]	
3D nitrogen and boron co-doped graphene	239 (1 A/g)	1 M H ₂ SO ₄	[25]	
Crumpled N-doped graphene nanosheets	245.9 (1 A/g)	BMIM BF ₄ /AN	[26]	
3D Nitrogen-doped graphene-CNT	180 (0.5 A/g)	6 M KOH	[27]	
Boron-doped graphene nanoplatelets	160 (1 A/g)	6 M KOH	[28]	
3D porous carbon	176 (10 mV s ⁻¹)	1 M H ₂ SO ₄	[29]	
GMP2NC	273 (0.2 A g ⁻¹)	6 M KOH	This work	

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