Electronic Supplementary Information (ESI)

Tetraphenylcyclopentadiene-Based Conjugated Microporous Polymers for High-Performance Energy Storage Carbons

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S1. Materials

All solvents and chemicals were obtained from commercial suppliers and used as received unless otherwise noted. Sodium sulphate (Na₂SO₄), potassium hydroxide (KOH), pyridine, benzil, malononitrile (CH₂CN₂), *o*-dichlorobenzene (*o*-DCB), titanium tetrachloride (TiCl₄), 1,3-diphenyl-2-propanone, 2,4,6-trichloro-1,3,5-triazine (TCT) and hexane were ordered from Sigma-Aldrich. Dichloromethane (DCM) and methanesulfonic acid were obtained from J. T. Baker. Tetrahydrofuran (THF, 99.9%) was ordered from Showa (Tokyo, Japan). Whereas, methanol (MeOH), and acetone were ordered from Alfa Aesar. Conc. HCl, and ethanol (EtOH) were obtained from ECHO chemical co. LTD.

S2. Characterization

Fourier-transform infrared spectroscopy (FTIR). FTIR spectra were recorded using a Bruker Tensor 27 FTIR spectrophotometer and the conventional KBr plate method; 32 scans were collected at a resolution of 4 cm^{-1} .

Solid state nuclear magnetic resonance (SSNMR) spectroscopy. SSNMR spectra were recorded using a Bruker Avance 400 NMR spectrometer and a Bruker magic-angle-spinning (MAS) probe, running 32,000 scans.

Thermogravimetric analysis (TGA). TGA was performed using a TA Q-50 analyzer under a flow of N₂. The samples were sealed in a Pt cell and heated from 40 to 800 °C at a heating rate of 20 °C min⁻¹ under N₂ at a flow rate of 50 mL min⁻¹.

Surface area and porosimetry (ASAP/BET). The BET surface areas and porosimetry investigations of the prepared samples (ca. 20–100 mg) were conducted using a Micromeritics ASAP 2020 Surface Area and Porosity analyzer. Nitrogen isotherms were generated through incremental exposure to ultrahigh-purity N_2 (up to ca. 1 atm) in a liquid N_2 (77 K) bath.

Field-emission scanning electron microscopy (FE-SEM). FE-SEM was performed using a JEOL JSM-7610F scanning electron microscope. Samples were subjected to Pt sputtering for 100 s prior to observation.

Transmission electron microscopy (TEM). TEM was accomplished using a JEOL-2100 scanning electron microscope, operated at 200 kV.

S3. Synthetic Procedures of Monomers



Scheme S1. Synthesis of 2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one (CP).

Synthesis of 2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one (CP) [S1]

To a 250 mL, two-neck round-bottom flask containing 175 mL of anhydrous ethanol and equipped with a condenser, septum and stir bar were added 1,3-(diphenyl)propan-2-one (4.00 g, 19.0 mmol, 1.02 eq) and benzil (3.92 g, 18.7 mmol, 1,00 eq). The solution was then refluxed for one hour. KOH (1.04 g, 18.7 mmol, 1.0 eq dissolved in 5 mL ethanol) was added dropwise to the warm solution through the septum using a syringe. The solution was refluxed for an additional 45 min before being cooled to 0 °C using an ice bath. After 2 h, the solution was filtered and the precipitate was washed twice with cold methanol to yield the CP monomer (7.17 g, 15.0 mol, 80.6%) as a purple crystalline powder. FTIR (cm⁻¹): 3054, 1709, 1487, 1442. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 6.95-7.21 (m, 20 H). ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 155.27, 133.75, 131.42, 130.81, 129.99, 129.97, 129.14, 128.63, 128.12, 128.10, 125.95.



Scheme S2. Synthesis of 2-(2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-ylidene) malononitrile (CPM).

Synthesis of 2-(2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-ylidene) malononitrile (CPM) [2]

TiCL₄ (2.2 mL, 3.8 g, 20 mmol) was added dropwise to an ice-cooled solution of tetraphenylcyclopentadienone (1.5 g, 3.9 mmol) and malononitrile (0.5 g, 7.5 mmol) in dichloromethane (50 mL) under nitrogen atmosphere. After the addition was complete, dry pyridine (7.5 mL) was added dropwise over 10 min. The reaction mixture was allowed to warm to room temperature and stirred under nitrogen overnight. The solution was cooled at 0 °C and HCl 10% (20 ml) was slowly dropped. The mixture was extracted with dichloromethane (50 mL × 3) and the organic phase was collected and dried with Na₂SO₄. After evaporation of the solvent, the crude was obtained as a green powder. The residue was purified by column chromatography, with hexane/dichloromethane 7:3 as eluent. The product was isolated as a green-yellow powder (1.5 g, 3.5 mmol, 44%). FTIR (cm⁻¹): 3024, 2214, 1483, 1439. ¹H NMR, (500 MHz, CDCl₃) ppm, δ : 6.87-7.34 (m, 20 H). ¹³CNMR, (125 MHz, CDCl₃) ppm, δ : 169.37, 151.88, 133.07, 132.39, 131.78, 130.45, 129.74, 129.36, 128.16, 111.84, 86.99.

S4. Synthetic Procedures of CMPs



Scheme S3. Synthesis of CP-TCT CMP.

A mixture of CP (1.2 mmol, 0.461 g) and 2,4,6-trichloro-1,3,5-triazine (TCT, 1.6 mmol, 0.295 g) in 16 mL dry o-dichlorobenzene and methane–sulfonic acid (22.4 mmol, 1.45 mL) was refluxed at 140 °C for 48 h. The precipitate filtered off from the hot reaction mixture was extracted overnight using a Soxhlet apparatus with methanol, tetrahydrofuran (THF) and acetone, then dried in vacuum. The target product was obtained as a grey solid with metallic luster (67.3% yield).



Scheme S4. Synthesis of CPM-TCT CMP.

A mixture of CPM (1.2 mmol, 0.519 g) and 2,4,6-trichloro-1,3,5-triazine (TCT, 1.6 mmol, 0.295 g) in 16 mL dry o-dichlorobenzene and methane–sulfonic acid (22.4 mmol, 1.45 mL) was refluxed at 140 °C for 48 h. The precipitate filtered off from the hot reaction mixture was extracted overnight using a Soxhlet apparatus with methanol, tetrahydrofuran (THF) and acetone, then dried in vacuum. The target product was obtained as a grey solid with metallic luster (53.5% yield).

S5. FTIR and NMR Spectral Profiles of Monomers



Figure S1. FTIR spectrum of 2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one (CP).



Figure S2. ¹H NMR spectrum of 2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one (CP).



Figure S3. ¹³C NMR spectrum of 2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one (CP).



Figure S4. FTIR spectrum of 2-(2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-ylidene)

malononitrile (CPM).



Figure S5. ¹H NMR spectrum of 2-(2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-ylidene)

malononitrile (CPM).



Figure S6. ¹³C NMR spectrum of 2-(2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-ylidene)

malononitrile (CPM).



Figure S7. FTIR spectra of (a) CP, (b) TCT, and (c) CP-TCT CMP.



Figure S8. FTIR spectra of (a) CPM, (b) TCT, and (c) CPM-TCT CMP.

S7. Thermal gravimetric analysis



Figure S9. TGA curves of (a) CP-TCT CMP, (b) CPM-TCT CMP, (c) CP-TCT-700, and (d) CPM-TCT-700.

Table S1. Values of $T_{d10\%}$ and Char yield of CMPs and their calcinated n	materials.
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СМР	Τ _{d10%} (°C)	Char yield (%)
СР-ТСТ	312 °C	62 %
CPM-TCT	517 °C	77 %
СР-ТСТ-700	598 °C	83 %
СРМ-ТСТ-700	471 °C	77 %



Figure S10. XPS spectra of (a) CP-TCT-700, and (b) CPM-TCT-700.



Figure S11. (a) XRD and (b) Raman spectra of CP-TCT-700 and CPM-TCT-700 carbon materials.



Figure S12. N_2 isotherms curves of (a) CP-TCT, and (b) CPM-TCT CMPs. Pore size

distribution curves of (c) CP-TCT, and (d) CPM-TCT CMPs.



Figure S13. SEM photos of (a) CP-TCT CMP, (b) CPM-TCT CMP, (c) CP-TCT-700 and (d) CPM-TCT-700; TEM photos of (e) CP-TCT CMP, (f) CPM-TCT CMP, (g) CP-TCT-700 and (h) CPM-TCT-700.

S8. Electrochemical Methods and Data

Working Electrode Cleaning: Prior to use, the glassy carbon electrode (GCE) was polished several times with 0.05-µm alumina powder, washed with EtOH after each polishing step, cleaned via sonication (5 min) in a water bath, washed with EtOH, and then dried in air.

Electrochemical Characterization: The electrochemical experiments were performed in a three-electrode cell using an Autolab potentiostat (PGSTAT204) and 1 M KOH as the aqueous electrolyte. The GCE was used as the working electrode (diameter: 5.61 mm; 0.2475 cm²). A Pt wire was used as the counter electrode; Hg/HgO (RE-61AP, BAS) was used as the reference electrode. All reported potentials refer to the Hg/HgO potential. The GCE was modified with CMP slurries, as described elsewhere, but with some modifications. [S3–S5] The slurries were prepared by dispersing the CMP (45 wt. %), carbon black (45 wt. %), and Nafion (10 wt. %) in EtOH (2 mL) and then sonicating for 1 h. A portion of this slurry (10 μ L) was pipetted onto

the tip of the electrode, which was then dried in air for 30 min prior to use. The electrochemical performance was studied through CV at various sweep rates (from 5 to 200 mV s⁻¹) and through the GCD method in the potential range from 0.0 to -1.0 V vs. Hg/HgO at various current densities (from 0.5 to 20 A g⁻¹) in 1 M KOH as the aqueous electrolyte solution. The specific capacitance was calculated from the GCD data using the following equation: [S5,S6]

$Cs = (I\Delta t)/(m\Delta V)$ [S7]

where Cs (F g⁻¹) is specific capacitance of the supercapacitor, I (A) is the discharge current, ΔV (V) is the potential window, Δt (s) is the discharge time, and m (g) is the mass of the CMP on the electrode. The energy density (E, W h kg⁻¹), and the power density (P, W kg⁻¹) were calculated using the following equations: [S8]

 $E = 1000C(\Delta V)^2 / (2*3600)$ [S9]

P = E/(t/3600) [S10]



Figure S14. (a) Ragone plots of the as-synthesized polymers and the corresponding calcinated microporous carbons. (b) Nyquist plots of cells incorporating the as-synthesized polymers.



Figure S15. (a) Bode plots of the frequency with respect to the resistance magnitude; (b) Bode plots of the frequency with respect to phase angle to determine the knee frequency for the assynthesized polymers and their corresponding calcinated microporous carbons.

Table S2. Comparison between the specific surface area and specific capacitance of the synthesized triazine-based CMPs with those of previously reported organic polymers for supercapacitor application.

Materials	$S_{BET}(m^2g^{-l})$	Capacitance	Ref.
Car-TPA COF	1334	13.6 F g^{-1} at 0.2 A g^{-1}	S3
Car-TPP COF	743	14.5 F g^{-1} at 0.2 A g^{-1}	S3
Car-TPT COF	721	$17.4 \text{ F g}^{-1} \text{ at } 0.2 \text{ A g}^{-1}$	S3
HOMCNSs	502	72.79 F g ⁻¹ at 0.5 A g ⁻¹	S11
An-CPOP-1	700	72.75 F g ⁻¹ at 0.5 A g ⁻¹	S12
An-CPOP-2	700	98.40 F $\rm g^{-1}$ at 0.5 A $\rm g^{-1}$	S12
TPE-HPP	922	$67 \text{ F g}^{-1} \text{ at } 0.5 \text{ A g}^{-1}$	S13
DPT-HPP	1230	110.5 F g^{-1} at 0.5 A g^{-1}	S13
Fc-CMPs	653.2	147 F g^{-1} at 0.5 A g^{-1}	S14
CMPs	672.3	72 F g^{-1} at 0.5 A g^{-1}	S14
Carbon nanotubes	988	98 F g^{-1} at 1 A g^{-1}	S15
Carbon nanoparticles	365	$84 \text{ F g}^{-1} \text{ at } 1 \text{ A g}^{-1}$	S16
DAB-TFP COF	385	98 F g^{-1} at 0.5 A g^{-1}	S17
СР-ТСТ-700	132	83 F g ⁻¹ at 1 A g ⁻¹	This work
СРМ-ТСТ-700	200	70 F g ⁻¹ at 1 A g ⁻¹	This work

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