Electronic Supplementary Information (ESI)

Engineering carbonyl-rich conjugated microporous polymers with a pyrene-4,5,9,10-tetraone building block as highly efficient and stable electrodes for energy storage

Ahmed F. Saber,^a Ya-Fan Chen,^b Levannie Mabuti,^b Swetha V. Chaganti,^c Santosh U. Sharma,^c Johann Lüder,^b Jyh-Tsung Lee,^c Shiao-Wei Kuo^b and Ahmed F. M. EL-Mahdy^{b,d*}

 ^aInterdisciplinary Research Center for Hydrogen Technologies and Carbon Management (IRCHTCM), King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia
^bDepartment of Materials and Optoelectronic Science, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan

^cDepartment of Chemistry, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan

^dChemistry Department, Faculty of Science, Assiut University, Assiut 71516, Egypt

*To whom correspondence should be addressed

E-mail: ahmedelmahdy@mail.nsysu.edu.tw

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S1. Materials

All solvents and chemicals were obtained from commercial suppliers and used as received unless otherwise noted. Ruthenium (III) chloride hydrate (RuCl₃·xH₂O, 99.95%), pyrene (Py, 98%), sodium periodate (NaIO₄, 99.8%), potassium permanganate (KMnO₄, ≥99.0%), potassium acetate (AcOK, 99%), 1,1'-bis(diphenylphosphino)ferrocene] dichloropalladium(II), bis(pinacolato)diboron (99%), concentrated sulfuric acid (H₂SO₄, 95-98%), chloroform (CHCl₃, \geq 99%), and hexane (\geq 99.7%) were ordered from Sigma-Aldrich. Dichloromethane (DCM, ≥99.8%), dimethyl formamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, \geq 99.9%), acetonitrile (MeCN, \geq 98%), and dioxane (\geq 99%) were obtained from J. T. Baker. Tetrahydrofuran (THF, 99.9%) was ordered from Showa (Tokyo, Japan). Tetrakis(triphenylphosphine)palladium (0) (99%) was purchased from Acros. Whereas bromine (Br₂, ≥98%), methanol (MeOH, 99.8%), acetone (≥99.5%), N-bromosuccinimide (NBS, 99%), and potassium carbonate (99%) were ordered from Alfa Aesar. Ethanol (EtOH, 99.5%), and ethyl acetate (\geq 99%) 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 2,7-dibromopyrene-4,5,9,10-tetraone (PT-2Br).

Synthesis of pyrene-4,5,9,10-tetraone (PT): [1]

Sodium periodate (45.0 g, 211 mmol), acetonitrile (103 mL), dichloromethane (DCM) (103 mL), H₂O (129 mL), Py (5.14 g, 25.70 mmol), and RuCl₃·xH₂O (0.64 g, 0.54 mmol) were charged in a dried round flask (500 mL). The solution mixture was stirred and kept at 40°C for 24 h, and the obtained suspension was washed several times with DCM. The yellow powder

was obtained after removing DCM under reduced pressure, and the solid was recrystallized using CHCl₃ (1.54 g, 23%). FTIR (cm⁻¹): 3060, 1675 (C=O), 1562, 1418, 1346, 1278, 1057, 913. ¹H NMR (500 MHz, DMSO-*d*₆, δ, ppm): 8.32 (4H), 7.74 (2H). ¹³C NMR (125 MHz, DMSO-*d*₆, δ, ppm): 178.43 (C=O), 134.88, 132.51, 130.92. HR-FD-MS: m/z: 263.032.

Synthesis of 2,7-dibromopyrene-4,5,9,10-tetraone (PT-2Br): [1]

PT (1.20 g, 4.56 mmol) was added to a cooled Schlenk flask, and then, 30 mL of concentrated H_2SO_4 and NBS (1.80 g, 10.20 mmol) was added to the flask, and the obtained solution was heated for 5 h at 50°C. The resulting yellow powder was purified by the recrystallization in DMSO and washed with DCM and ether to afford PT-Br₂ as a yellow solid (1.26 g, 68%). FTIR (cm⁻¹): 3070, 1679 (C=O), 1545, 1421, 1260. ¹H NMR (500 MHz, DMSO-*d*₆, δ , ppm): 8.36 (4H). ¹³C NMR data of PT-Br₂ is not provided due to its poor solubility. HR-FD-MS: m/z: 421.328.



Scheme S2. Synthesis of 3,3',6,6'-tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9'-bicarbazole (BC-4BO).

Synthesis of 3,3',6,6'-Tetrabromo-9,9'-bicarbazole (BC-4Br): [2]

Potassium permanganate (2.92 g, 90 mmol) was added to a solution of 3,6-dibromocarbazole (2 g, 30 mmol) in 40 mL acetone at 50°C. Then the solution was hydrolyzed with 100 mL distilled water. The mixture was extracted with dichloromethane and the solvent was evaporated. The residue was washed with methanol to yield 3,3',6,6'-tetrabromo-9,9'-bicarbazole (6.92 g, 71%). ¹H NMR (500 MHz, CDCl₃, δ , ppm): 8.27 (d, 4 H), 7.47 (dd, J =

8.5 Hz, 4H), 6.75 (d, J = 8.5 Hz, 4H). ¹³C NMR (125 MHz, CDCl₃, δ, ppm): 139.31, 131.19, 124.81, 123.30, 115.41, 110.59.

Synthesis of 3,3',6,6'-tetraboronic-pinacolate-9,9'-bicarbazole (BC-4BO): [2]

A mixture of BC-4Br (1.87g, 2.90 mmol), bis(pinacolate)diboron (4.4 g, 17.35 mmol), [1,1'bis(diphenylphosphino)ferrocene] dichloropalladium(II) (183 mg, 0.25 mmol) and potassium acetate (1.75 g, 17.85 mmol) were heated at reflux in dioxane at 100°C for two days under N₂ atmosphere. The solution was poured into a stirred beaker filled with ice cubes and H₂O. The product was extracted with DCM then purified chromatographically through (SiO₂; hexane/EtOAc, 3:1) to give BC-4BO as a white precipitate (2.18 g, 90 %). FTIR (cm⁻¹): 2977, 2929, 2862,1602, 1345, 1456, 1148, and 1080. ¹H NMR (500 MHz, CDCl₃, δ , ppm): 8.70 (s, 4H), 7.71 (d, J = 10.0 Hz, 4H), 6.80 (d, J = 10.0 Hz, 4H), 1.32 (s, 48H). ¹³C NMR (125 MHz, CDCl₃, δ , ppm): 141.65, 133.11, 128.58, 121.58, 108.12, 88.47, and 24.16.



Scheme S3. Synthesis of N¹,N¹,N⁴,N⁴-tetrakis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)benzene-1,4-diamine (TPA-4BO).

Synthesis of N^1 , N^1 , N^4 , N^4 -tetrakis(4-bromophenyl)benzene-1,4-diamine (TPA-4Br): [2] N^1 , N^1 , N^4 , N^4 -tetraphenylbenzene-1,4-diamine (TPA, 1 g, 2.37 mmol) was dissolved in dry DMF (40 L) in a 50 mL round-bottom flask, and the solution was cooled to 0°C using an ice bath. After that, an injection of *N*-bromosuccinimide (NBS, 1.94 g, 10.8 mmol) dissolved in dry DMF (20 mL) was performed, and the resultant solution was stirred at 0°C for 30 minutes.

The solution was then stirred at room temperature overnight before being placed onto ice water. The resultant precipitate was recovered through filtration and washed multiple times with ethanol. The product was dried at 60°C for overnight to yield 1.04 g (1.64 g, 93%) of TPA-4Br as white powder. FTIR (cm⁻¹): 1576, 1499, and 1016.

Synthesis of *N¹*,*N¹*,*N⁴*,*N⁴*-tetrakis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)phenyl)benzene-1,4-diamine (TPA-4BO): [2]

A mixture of TPA-4Br (1.2 g, 5.8 mmol), bis(pinacolate)diboron (2.6 g, 35.96 mmol), [1,1'bis(diphenylphosphino) ferrocene] dichloropalladium (II) (105 mg, 0.5 mmol) and potassium acetate (0.5 g, 35,7 mmol) were heated at reflux in dioxane (50 mL) at 100°C for two days under N₂ atmosphere. The solution was poured into a stirred beaker filled with ice cubes and H₂O. The resultant precipitate was recovered through filtration, washed multiple times with ethanol, and then purified chromatographically through (SiO₂; hexane/THF, 7:3) to give TPA-4BO as a white precipitate (1.33 g, 88 %). FTIR (cm⁻¹): 2979, 2931, 2857, 1601, 1501, 1353, and 1144. ¹H NMR (500 MHz, DMSO-d₆, δ , ppm): 7.17 (d, J = 8.0 Hz, 8H), 7.06 (d, J = 8.0 Hz, 8H), and 6.96 (d, J = 8.0 Hz, 4H). m/z (EI, 70 eV) 913.50, 914.52, 915.54, 916.51, 917.52, and 918.51.

S4. Synthetic Procedures of CMPs



Scheme S4. Synthesis of BC-PT CMP.

Synthesis of BC-PT CMP

In a 25 mL Pyrex tube, a mixture of BC-4BO (150 mg, 0.179 mmol), PT-2Br (150.68 mg, 0.359 mmol), tetrakis(triphenylphosphine)palladium (41.46 mg, 0.036 mmol), and potassium carbonate (495.8 mg, 3.59 mmol) was evacuated for 10 mins. Then a co-solvent of DMF and H_2O (5:1, v/v, 12 mL) was added. Degassing of the reaction mixture by freeze–pump–thaw cycles and purging with N_2 was carried out and the closed tube was then stirred at 145°C for 72 hrs. After allowing the mixture to cool at 25°C, the formed precipitate was isolated *via* centrifuging, thoroughly washed sequentially with water, methanol, acetone, and tetrahydrofuran till colorless solution, and extracted by Soxhlet sequentially with methanol ethanol, hexane and tetrahydrofuran for 96 h. Finally, the obtained precipitate was dried at 120°C for 16 h under vacuum to yield BC-PT CMP as a black solid (75% yield).



Scheme S5. Synthesis of TPA-PT CMP.

Synthesis of TPA-PT CMP

In a 25 mL Pyrex tube, a mixture of TPA-4BO (164 mg, 0.179 mmol), PT-2Br (150.68 mg, 0.359 mmol), tetrakis(triphenylphosphine)palladium (41.46 mg, 0.036 mmol), and potassium carbonate (495.8 mg, 3.59 mmol) was evacuated for 10 mins. Then a co-solvent of DMF and H_2O (5:1, v/v, 12 mL) was added. Degassing of the reaction mixture by freeze–pump–thaw cycles and purging with N₂ was carried out and the closed tube was then stirred at 125°C for 72 hrs. After allowing the mixture to cool at 25°C, the formed precipitate was isolated *via* centrifuging, thoroughly washed sequentially with water, methanol, acetone, and tetrahydrofuran till colorless solution, and extracted by Soxhlet sequentially with methanol, ethanol, hexane and tetrahydrofuran for 96 h. Finally, the obtained precipitate was dried at 120°C for 16 h under vacuum to yield TPA-PT CMP as a black solid (76% yield).



Figure S1. FTIR spectra of (a) BC-4BO, (b) PT-2Br, and (c) BC-PT CMP.



Figure S2. FTIR spectra of (a) TPA-4BO, (b) PT-2Br, and (c) TPA-PT CMP.



Figure S3. TGA curves of (a) BC-PT CMP, and (b) TPA-PT CMP.

Table S1. Values of $T_{d10\%}$ and Char yield of the synthesized CMPs.

СМР	Τ _{d10%} (°C)	Char yield (%)
BC-PT CMP	443°C	73%
ТРА-РТ СМР	424°C	74%



Figure S4. Solubility experiment of (a) BC-PT and (b) TPA-PT CMPs in different solvents.

S8. X-Ray Diffraction (XRD)



Figure S5. XRD analysis of the BC-PT and TPA-PT CMPs.

S9. SEM-EDS Mapping



Figure S6. SEM image and EDS elemental mapping photos for BC-PT CMP.



Figure S7. SEM image and EDS elemental mapping photos for TPA-PT CMP.

S10. TEM-EDX analysis

a)				(b)			
	Element	At. %		С	Element	At. %	
	С	62.31			С	60.95	
,	N	21.01			N	25.93	
	0	14.29			0	12.02	
	Pd	1.39			Pd	1.10	
				N			
N							
0				O			
Pd				Pd			
2 4	6 8 10	12	14	0 2 4	6 8 10	12	14

Figure S8. EDX elemental analysis for (a) BC-PT and (b) TPA-PT CMPs.

S11. ICP-OES analysis

Table S2.	The	palladium	content in	the s	vnthesized	CMPs.
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Polymers	Raw data	Dilution ratio in machine	Concentration (ppm)	RSD (%)
ВС-РТ СМР	0.3016	10	3.016	0.21
ТРА-РТ СМР	0.2158	10	2.158	0.16

S12. 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: [S3,S4]

$$Cs = (I\Delta t)/(m\Delta V)$$
 [S5]

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: [S6]

$$E = 1000C(\Delta V)^2 / (2*3600)$$
 [S7]

$$P = E/(t/3600)$$
 [S8]

We evaluated the electrochemical functionality of a symmetric supercapacitor using a CR2032 coin cell, which consists of an anode and cathode, a bottom and top cover, a metal spring, a separator, and an electrolyte. Our compounds served as both the cathode and the anode to construct a symmetric supercapacitor. The slurry was created by combining 2 mg of CMP, 2 mg of conductive carbon, 20 mL of Nafion, 200 mL of ethanol, and 400 mL of water. It was

then sonicated for an hour and cast onto carbon paper. We used a Selemion AMV membrane with an electrolyte of 1.0 M aqueous KOH.

The specific capacitance was calculated in assembled supercapacitor from the GCD data using the following equations:

$$Cs = 2(I\Delta t)/(m\Delta V)$$

where Cs (F g⁻¹) is the 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 in the single electrode.

The energy density (E, W h kg⁻¹) and power density (P, W kg⁻¹) were calculated using the equations:

 $E_{cell} = 1000 \text{ Cs} (\Delta V)2/(4 \cdot 2 \cdot 3600)$

and

 $P_{cell} = E_{cell} / (t/3600)$



Figure S9. (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 in three-electrode system.



Figure S10. (a) Nyquist plots of three electrode system for BC-PT and TPA-PT CMPs before and after fitting, (b) Equivalent fitting circuit.



Figure S11. The relative contributions of capacitive and diffusion currents of (a) BC-PT, and (b) TPA-PT polymers, recorded at 10 mV.



Figure S12. (a) Bode plot of the frequency with respect to the resistance magnitude; (b) Bode plot of the frequency with respect to phase angle to determine the knee frequency for the assynthesized BC-PT polymer in coin cell system.



Figure S13. (a) Nyquist plot of device system for BC-PT CMP before and after fitting, (b) Equivalent fitting circuit.

Table S3. Comparison between the specific surface area and specific capacitance of the synthesized PT-based CMPs with those of previously reported organic polymers for three

electrodes supercapacitor application.

Materials	$S_{BET}(m^2 g^{-1})$	Capacitance	Current density	Ref.
		$(F g^{-1})$	$(A g^{-1})$	
Car-TPA COF	1334	13.6	0.2	S9
Car-TPP COF	743	14.5	0.2	S9
Car-TPT COF	721	17.4	0.2	S9
HOMCNSs	502	72.79	0.5	S10
An-CPOP-1	700	72.75	0.5	S11
An-CPOP-2	700	98.40	0.5	S11
TPE-HPP	922	67	0.5	S12
DPT-HPP	1230	110.5	0.5	S12
Fc-CMPs	653.2	147	0.5	S13
Carbon nanotubes	988	98	1.0	S14
Carbon nanoparticles	365	84	1.0	S15
DAB-TFP COF	385	98	0.5	S16
CoPc-CMP	150.7	13.8	1.0	S17
TAT-CMP-1	88	141	1.0	S18
TAT-CMP-2	106	183	1.0	S18
BC-PT CMP	478	373	1.0	This work
TPA-PT CMP	232	204	1.0	This work

S13. Density Functional Theory (DFT) Calculations



Figure S14. (a,d) The optimized geometry, (b,e) the HOMO orbitals, and (c,f) LUMO orbitals of the (a-c) BC-PT and (d-f) TPA-PT polymers. An iso-contour value of 0.02 $e^{1/2}/A^{3/2}$ was chosen. (g) and (h) give structural details of BC-PT and TPA-PT, respectively. Color code: white: hydrogen atoms, cyan: carbon atoms, blue: nitrogen atoms, red: oxygen atoms.



Figure S15. (a) The computed quantum capacitance of TPA-PT and BC-PT with T=300 K and (b) the density of states of TPA-PT and BC-PT with a Gaussian broadening of $\sigma = 250 \text{ meV}$. Note that the curve in (a) were obtained after alignment of the curves in (b) at the Fermi energy taken as onset of the HOMO peak. The vertical solid line indicates the HOMO position, and the vertical dotted line indicates the LUMO position in (b).

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