Supporting Information for

Dispersions of Ultrastable Crown-Ether Functionalized Triphenylamine and Pyrene-Linked Porous Organic Conjugated Polymers with Single-Walled Carbon Nanotube as the High-Performance Electrode for Supercapacitor

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Characterization

FTIR spectra were collected on a Bruker Tensor 27 FTIR spectrophotometer with a resolution of 4 cm⁻¹ by using the KBr disk method. ¹³C nuclear magnetic resonance (NMR) spectra were examined by using an INOVA 500 instrument with DMSO as the solvent and TMS as the external standard. Chemical shifts are reported in parts per million (ppm). The curing behavior and thermal stabilities of the samples were performed by using a TG Q-50 thermogravimetric analyzer under a N₂ atmosphere; the cured sample (ca. 5 mg) was put in a Pt cell with a heating rate of 20 °C min⁻¹ from 100 to 800 °C under a N₂ flow rate of 60 mL min⁻¹. Wide-angle X-ray diffraction (WAXD) patterns were measured by the wiggler beamline BL17A1 of the National Synchrotron Radiation Research Center (NSRRC), Taiwan. A triangular bent Si (111) single crystal was used to get a monochromated beam having a wavelength (λ) of 1.33 Å. The morphologies of the polymer samples were examined by Field emission scanning electron microscopy (FE-SEM; JEOL JSM7610F) and also by transmission electron microscope (TEM) using a JEOL-2100 instrument at an accelerating voltage of 200 kV. BET surface area and porosimetry measurements of samples (ca. 40–100 mg) were measured using BEL MasterTM/BEL simTM (v. 3.0.0). N₂ adsorption and desorption isotherms were generated through incremental exposure to ultrahigh-purity N₂ (up to ca. 1 atm) in a liquid N2 (77 K) bath. Surface parameters were calculated using BET adsorption models in the instrument's software. The pore size of the prepared samples was determined by using nonlocal density functional theory (NLDFT).

Electrochemical Analysis

Working Electrode Cleaning: Prior to using, the glassy carbon electrode (GCE) was polished several times with 0.05-µm alumina powder, washed with EtOH after each polishing step, cleaned through 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-1B, BAS) was the reference electrode. All reported potentials refer to the Hg/HgO potential. A slurry was prepared by dispersing CE-Py POP and CE-Py POP/SWCNT nanocomposite (2 mg), carbon black (2 mg), and Nafion (10 wt%) in a mixture of (EtOH/ H₂O) (200 μ L: 800 μ L) 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 (5–200 mV s⁻¹) and through the GCD method in the potential range from -1.0 V and 0.0 V (vs. Hg/HgO) at various current densities (0.5–20 A g⁻¹) in 1 M KOH as the aqueous electrolyte solution.

The specific capacitance was calculated from the GCD data using the equation.

 $C_{\rm s} = (I\Delta t)/(m\Delta V)$

Where C_s (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 NPC on the electrode. The energy density (*E*, W h kg⁻¹) and power density (*P*, W kg⁻¹) were calculated using the equations.

 $E = 1000C(\Delta V)^2/(2 \times 3600)$

P = E/(t/3600)





Full Scale 172 cts Cursor: 0.000

keV

0 Ka1

Figure S1. SEM-EDS mapping of CE-Py POP.



Figure S2. (a) N₂ adsorption/desorption isotherms, and (b) pore size distributions of CE-Py POP, SWCNT and CE-Py POP/SWCNT.



Figure S3. (a) CV, and (b) GCD of SWCNT.



Figure S4. Ragone profile of CE-Py POP and CE-Py POP/SWCNT (three electrodes system).



Figure S5. Ragone plots of CE-Py POP/SWCNT-AS (device) nanocomposite.

Table S1. Comparison the specific capacitance of CE-Py POP and CE-Py POP/SWCNT nanocomposite with those of previously reported materials for supercapacitor application.

Electrode	Capacitance	Ref.
СЕ-Ру РОР	122 F g^{-1} at 0.5 A g^{-1}	This work
CE-Py POP/SWCNT	346 F g^{-1} at 0.5 A g^{-1}	This work
Cz-Cz CMP	43.70 F g^{-1} at 0.5 A g^{-1}	S1
Cz-TP CMP	67.38 F g ⁻¹ at 1 A g ⁻¹	S1
POSS-F-POIP	36.2 F g^{-1} at 0.5 A g^{-1}	S2
H-THAQ	15 F g ⁻¹ at 1 A g ⁻¹	S3
THAQ/rGO (2:1)	76 F g ⁻¹ at 1 A g ⁻¹	S3
Pure AQ	42 F g^{-1} at 1 A g^{-1}	S4
TPE-DDSQ-POIP	22 F g ⁻¹ at 1 A g ⁻¹	S5
Car-DDSQ-POIP	23 F g ⁻¹ at 1 A g ⁻¹	S5
OVS-A HPP	120 F g ⁻¹ at 0.5 A g ⁻¹	S6
OVS-P-A HPP	177 F g ⁻¹ at 0.5 A g ⁻¹	S 6
Py-PDT POP	28 F g ⁻¹ at 0.5 A g ⁻¹	S7
TBN-BSU CMP	70 F g ⁻¹ at 0.5 A g ⁻¹	S8
Py-BSU CMP	38 F g ⁻¹ at 0.5 A g ⁻¹ S8	
N- doped Porous carbons ropes	60 F g ⁻¹ at 1.0 A g ⁻¹ S8	
TPE-FFC-CMP/CD-BZ	7.53 F g ⁻¹ at 0.5 A g ⁻¹	S9
TPE-FFC-CMP/poly (CD-BZ)	37.07 F g ⁻¹ at 0.5 A g ⁻¹	S9
Py-FFC-CMP/CD-BZ	10.15 F g ⁻¹ at 0.5 A g ⁻¹	S9
Py-FFC-CMP/poly (CD-BZ)	46 F g ⁻¹ at 0.5 A g ⁻¹	S 9
HPC-0	48 F g ⁻¹ at 1 A g ⁻¹	S10
Н-ТНАQ	$15 \text{ F g}^{-1} \text{ at } 1 \text{ A g}^{-1}$	S11
poly(TPA-DHTP-BZ) POP	67.1 F g ⁻¹ at 0.5 A g ⁻¹	S12
TPA-OXD-CMP/SWCNT	360 F g ⁻¹ at 0.5 A g ⁻¹	S13
TBN-TPE-CMP/SWCNT	156 F g ⁻¹ at 0.5 A g ⁻¹ S14	

TBN-Car-CMP/SWCNT	53 F g ⁻¹ at 0.5 A g ⁻¹	S14
CuTAPP-CMP/CNTs-1	70 F g ⁻¹ at 1 A g ⁻¹	S15
CuTAPP-CMP/CNTs-2	31 F g ⁻¹ at 1 A g ⁻¹	S15
CuTAPP-CMP/CNTs-3	207.8 F g ⁻¹ at 1 A g ⁻¹	S15
CuTAPP-CMP/CNTs-4	47.7 F g^{-1} at 1 A g^{-1}	S15
CoCP/CNTs	31.5 F g^{-1} at 1 A g^{-1}	S16
CoCP-CMP/CNTs	212 F g ⁻¹ at 1 A g ⁻¹	S16

Sample	Rs (Ω)	Rct (Ω)	CPE-EDL (S·s ⁿ)	$CPE-P(S \cdot s^n)$
СЕ-Ру РОР	6.54	26.30	0.0000605	0.000026
CE-Py POP/SWCNT	5.60	10.43	0.0000026	0.000078
CE-Py POP/SWCNT- AS (device)	39.13	76.80	0.00000006	0.00104

Table S2. Characteristics of Fitted Nyquist Plots of the POP-CMPs.

References

[S1] S.F. Saber, S.U. Sharma, J.T. Lee, A.F.M. EL-Mahdy, S.W. Kuo, Carbazoleconjugated microporous polymers from Suzuki–Miyaura coupling for supercapacitors, Polymer 254 (2022) 125070. doi.org/10.1016/j.polymer.2022.125070.

[S2] M.G. Mohamed, T.H. Mansoure, Y. Takashi, M.M. Samy, T. Chen, S.W. Kuo, Ultrastable porous organic/inorganic polymers based on polyhedral oligomeric silsesquioxane (POSS) hybrids exhibiting high performance for thermal property and energy storage, Microporous Mesoporous Mater. 328 (2021) 111505. doi.org/10.1016/j.micromeso.2021.111505.

[S3] L. Xu, R. Shi, H. Li, C. Han, M. Wu, C.P. Wong, F. Kang, B. Li, Pseudocapacitive anthraquinone modified with reduced graphene oxide for flexible symmetric all-solidstate supercapacitors, Carbon 127 (2018) 459-468. doi.org/10.1016/j.carbon.2017.11.003.

[S4] B. Guo, Y. Yang, Z. Hu, Y. An, Q. Zhang, X. Yang, X. Wang, H. Wu, Redoxactive organic molecules functionalized nitrogen-doped porous carbon derived from metal-organic framework as electrode materials for supercapacitor, Electrochim. Acta, 223 (2017) 74–84. doi.org/10.1016/j.electacta.2016.12.012.

[S5] M.G. Mohamed, W.C. Chen, A.F.M. EL-Mahdy, S.W. Kuo, Porous organic/inorganic polymers based double-decker silsesquioxane for on high-performance energy J. Polym. Res. 28 (2021)219. storage, doi.org/10.1007/s10965-021-02579-x.

[S6] M. Ejaz, M.M. Samy, Y. Ye, S.W. Kuo, M.G. Mohamed, Design Hybrid Porous Polyhedral Organic/Inorganic Containing Polymers Oligomeric Silsesquioxane/Pyrene/Anthracene Moieties as a High-Performance Electrode for J. Sci. 24 Supercapacitors, Int. Mol. (2023)2501. https://doi.org/10.3390/ijms24032501.

[S7] A.O. Mousa, M.G. Mohamed, C.H. Chuang, S.W. Kuo, Carbonized Aminal-Linked Porous Organic Polymers Containing Pyrene and Triazine Units for Gas Uptake and Energy Storage, Polymers 15 (2023) 1891. doi.org/10.3390/polym15081891.

[S8] M.G. Mohamed, S.Y. Chang, M. Ejaz, M.M. Samy, A.O. Mousa, S.W. Kuo, Design and Synthesis of Bisulfone-Linked Two-Dimensional Conjugated Microporous Polymers for CO₂ Adsorption and Energy Storage, Molecules 28 (2023) 3234. doi.org/10.3390/molecules28073234.

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[S8] P. Thirukumaran, A. Parven, Y.R. Lee, S.C. Kim, Polybenzoxazine originated Ndoped mesoporous carbon ropes as an electrode material for high-performance supercapacitors, J. Alloys Comp., 750 (2018) 384-391. doi.org/10.1016/j.jallcom.2018.04.034.

[S9] M.M. Samy, M.G. Mohamed, T.H. Mansoure, T.S. Meng, M.A.R. Khan, C.C. Liaw, S.W. Kuo, Solid state chemical transformations through ring-opening polymerization of ferrocene-based conjugated microporous polymers in host–guest complexes with benzoxazine-linked cyclodextrin, J. Taiwan Inst. Chem. Eng., 132 (2022) 104110. DOI: 10.1016/j.jtice.2021.10.010.

[S10] L. Wan, J. Wang, L. Xie, Y. Sun, K. Li, Nitrogen-enriched hierarchically porous carbons prepared from polybenzoxazine for high-performance supercapacitors, ACS Appl. Mater. Interfaces, 6 (2014) 15583–15596. DOI: 10.1021/am504564q.

[S11] L. Xu, R. Shi, H. Li, C. Han, M. Wu, C.P. Wong, F. Kang, B. Li, Pseudocapacitive anthraquinone modified with reduced graphene oxide for flexible symmetric all-solid-state supercapacitors, Carbon 127 (2018) 459-68. DOI: 10.1016/j.carbon.2017.11.003.

[S12] M. Ejaz, M.G. Mohamed, S.W. Kuo, Solid state chemical transformation provides a fully benzoxazine-linked porous organic polymer displaying enhanced CO₂ capture and supercapacitor performance. Polym. Chem., 14 (2023) 2494-2509. doi.org/10.1039/D3PY00158J.

[S13] M.G. Mohamed, M.M. Samy, T.H. Mansoure, S.U. Sharma, M.S. Tsai, J.H. Chen, J.T. Lee, S.W Kuo, Dispersions of 1,3,4-Oxadiazole-Linked Conjugated Microporous Polymers with Carbon Nanotubes as a High-Performance Electrode for Supercapacitors, ACS Appl. Energy Mater. 5 (2022) 3677–3688. https://doi.org/10.1021/acsaem.2c00100. [S14] M.M. Samy, M.G. Mohamed, A.F.M. EL-Mahdy, T.H. Mansoure, K.C.W. Wu,
S.W. Kuo, High-performance supercapacitor electrodes prepared from dispersions of tetrabenzonaphthalene-based conjugated microporous polymers and carbon nanotubes,
ACS Appl. Mater. Interfaces 13 (2021) 51906-51916.
https://doi.org/10.1021/acsami.1c05720.

[S15] L. Mei, J.C. Wei, Q. Duan, Construction of copper porphyrin-linked conjugated microporous polymer/carbon nanotube composite as flexible electrodes for supercapacitors. J. Mater. Sci. Mater. Electron. 32 (2021) 24953–24963. doi.org/10.1007/s10854-021-06952-w.

[S16] L. Mei, X. Cui, Q. Duan, Y. Li, X. Lv, H.G. Wang, Metal Phthalocyanine Linked Conjugated Microporous Polymer Hybridized with Carbon Nanotubes as a High-Performance Flexible Electrode for Supercapacitors. Int. J. Hydrogen Energy, 45 (2020) 22950-22958. doi.org/10.1016/j.ijhydene.2020.06.208.