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Supporting Information

A Two-Dimensional Conjugated Polymer Framework with Fully

*sp*²-bonded Carbon Skeleton

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Synchrotron X-ray diffraction on powder samples

High-resolutionpowder diffraction experiments were recorded onBeamline BL16B1 at Shanghai Synchrotron Radiation Facility, SSRF. The samplewas held in1 mm capillary. A MarCCD detector was used. *q* calibration and linearization were verified using several orders of layer reflections from silver behemate. The measurement of the positions of the diffraction peaks was carried out using Galactic PeakSolveTM program, where experimental diffractograms are fitted using Gaussian shaped peaks. The diffraction peaks are indexed on the basis of their peak positions, and the lattice parameter and the plane group are subsequently determined.

Structural Modelling and Powder X-Ray Diffraction Analysis

Molecular modeling of 2DPPVwas generated using the Accelrys Material Studio software package. Prof. Yumei Zhang at the College of Materials Science and Engineering, Donghua University, China, allowed us to use their software package to carry out this part of the work.

The initial lattice was created by starting with the space group of *Cmcm*, with the parameters of a= 6.35 nm, b= 3.62 nm and c= 1.40 nm determined by PXRD experiment. Firstly, we degraded the symmetry of the lattice to P1, inserted the optimized monomer in the empty cell, omitted the redundant carbon atoms and all the hydrogen atoms, and then promoted the symmetry to *Cmcm*, outputting the crude structure of 2DPPV. Then the lattice model was geometry optimized using the MS Forcite molecular dynamics module (Universal force fields, Ewald summations). Finally, Pawley refinement was applied to define the lattice parameters, producing the refined PXRD profile with a lattice parameter of a = 6.32 nm, b = 3.57 nm c = 1.39 nm with R_{wp} and R_p values converged to 3.40% and 7.12%, respectively(Fig. 2a and S12).

Similarly, aneclipsed and staggeredarrangement for 2DPPVwere also examined (Figs. S14 and S16). For eclipsed arrangement, a PXRD pattern with a = b = 3.66 nm and c = 0.36 nm, R_{wp} and R_p values converged to 5.39% and 2.94% respectively was also obtained. Overlay of the observed and refined profiles shows good agreement (Fig.2d and S15). The PXRD pattern calculated for the staggeredarrangement did not match the observed pattern very well (Fig. 2f and S17), possibly ruling sucharrangement out.

Electrochemical Capacity (Supercapacitor) Measurement:

Electrochemical capacity characterizations were conducted on an EG &potentiostat/galvanostat Model 2273 advanced electrochemical system. Aconventional cell with a three-electrode configuration was employed throughout thisstudy. Working electrode was prepared by mixing 2DPPV-X (X=700, 800 and 900) with carbon black(Mitsubishi Chemicals, Inc.) and poly-tetrafluoroethylene (PTFE) binder. The weightratio of the sample, carbon black and PTFE was 80:10:10. A platinum foil wasapplied as a counter electrode with a Ag/AgCl electrode as a reference electrode. Theexperiments were carried out in 6 M KOH solution. The potential range was between-

0.8 to 0 V (Ag/AgCl) at different scan rates at the ambient temperature.

Electrochemical catalysed oxygen reduction reaction performance:

The working electrode was prepared by loading a catalyst sample film of 0.60 mg cm⁻² onto a glass carbon electrode. First, the ink was prepared by dispersing 10 mg of catalyst (2DPPV-800a) in 500 μ L of 1 wt % Nafion ethanol solution, and then sonicatingfor at least 30 min to form a homogeneous dispersion. Next, 6 μ L of the catalyst inkwas loaded onto a glassy carbon electrode with a diameter of 5 mm(0.6 mg/cm²).Pt/C ink was prepared by dispersing 4 mg of Pt/C (20 wt% Pt) in 1 mL of ethanol with 35 μ L of 5 wt% Nafion solution (40 wt% of Nafion to catalyst ratio), and then 5 μ L of Pt/C inkwas loaded onto a glassy carbon electrode. The ink was dried slowly in air, and the drying condition was adjusted by trial and error until a uniform catalyst distribution across the electrode surface was obtained.

Electrochemical measurements of cyclic voltammetry, rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) were performed by a basic bipotentiostat (Pine Research Instrumentation, USA) with a three-electrode cell system. A rotating glass carbon disk and platinum ring electrode (Pine Research Instrumentation, USA) after loading the electrocatalyst was used as the working electrode, an Ag/AgCl (KCl, 3 M) electrode as the reference electrode, and a Pt wire as the counter electrode. The electrochemical experiments were conducted in O_2 saturated 0.1 M KOH electrolyte for the oxygen reduction reaction. The potential range was cyclically scanned between -1.0 and +0 V at a scan rate of 100 mV/s at the room temperature after purging O_2 gas for 30 min. RDE measurements were conducted at different rotating speeds from 225 to 2500 rpm.

Rotating Ring-Disk Electrode (RRDE) Measurement:

Catalyst inks and electrodes were prepared by the same method as above. The disk electrode was scanned cathodically at a rate of 5 mV s⁻¹, and the ring potential was constant at 0.5 V vs. Ag/AgCl.

Based on the RRDE result, the $HO_2^{-}(\%)$ and the electron transfer number (*n*) were determined by the following equations:

$$n = \frac{4I_{Disk}}{I_{Disk} + \frac{I_{Ring}}{N}}$$
(S1)
%(HO₂⁻) = $\frac{200 \times \frac{I_{Ring}}{N}}{I_{Disk} + \frac{I_{Ring}}{N}}$ (S2)

where I_{disk} is disk current, I_{ring} is ring current, and N is current collection efficiency of the Pt ring, which was provided as 0.37 by manufacture. The glassy carbon electrode with a diameter of 5.61 mm was used in this experiment.



Scheme S1. Proposed mechanism of the Knoevenagel condensation reaction. In the first step, deprotonation can be realized by using a base (such as piperidine, Cs_2CO_3 , etc.) as catalyst to produce cyano group stabilized carbon anion. Then, C-C bond can be formed after nucleophilic substitution. At last, following an elimination, unsaturated olefin bond is produced.



Fig. S1 Thermogravimetricanalysis curve of 2DPPV. The 2DPPV shows high thermal stability up to 400 °C, and it has high carbon yield (68.9%) at 800 °C.



Fig. S2 FTIR spectra of 2DPPV and the monomers. The observation of transmittance peak at 2250 cm⁻¹ in the FTIR spectra of1, 4-phenylenediacetonitrile(M2) and 2DPPVreveals the existence of -C=N group.¹ The peak with high intensity at 1693 cm⁻¹ can be ascribed to -C=O stretch for the aromatic aldehyde monomer M1. Most importantly, the signal at 3020 cm⁻¹ which is attributable to C=CH, was found for the as-synthesized 2DPPV.No – C=O stretch signal was observed for 2DPPV, indicating that the olefin bridge moieties were built within the framework of 2DPPV.



Fig. S3 Solid-state ¹³C NMR spectra and XPS spectra of 2DPPV (a, b, c). The peaks at 141 and 127 ppm can be assigned to the carbons in the olefin linkage with H substituent and aromatic rings, respectively (see Fig. S3a), while the peak at 110 ppm, which should be attributed to the carbon in CN group, is weak. A heavy overlap hampers the assignment of individual signals. From the C1s spectra, aromatic/olefin carbon ($284.5\pm0.1 \text{ eV}$) and the cyano carbon ($286.0\pm0.5 \text{ eV}$) were found (Fig. S3b) for 2DPPV. Besides, the N1s binding energy at $398.0\pm0.1 \text{ eV}$ can be ascribed to the nitrogen in cyano group for 2DPPV(Fig. S3c).



Fig. S4 Optical microscope images of 2DPPV.The crystals vary in size between several and hundreds microns.



Fig. S5 SEM images of 2DPPV. Similar to optical microscope images, there are plenty of sheet-like flakes in the field of vision.



Fig. S6 AFM images and height analysis of 2DPPV. The thickness of three typical sheetlike flakes were measured by AFM technique. As shown in the height profiles, the thickness varies between 50-300 nm.



Fig. S7 SEM images of 2DPPV after ball milling. Thinner and large area of the staked sheets can be be be with the SEM images.



Fig. S8 HR-TEM images of 2DPPV. Both of the edges (b-d) and the bulk phase (a) of 2DPPV show obvious layered domains.



Fig. S9 Detailed PXRD analysis of 2DPPV: (a) the orthorhombic lattice with some of possible indexations; (b) the hexagonal lattice with full indexations.



Fig. S10. PXRD patterns of the building blocks used for the preparation of 2DPPV. The diffraction peaks from the two key building blocks could not be found in the PXRD pattern of 2DPPV (see Fig. 2), therefore, the co-crystallization of the building blocks with the COF structure did not occur under the experimental conditions.



Fig.S11 Unit cell (a) and serrated crystal lattice packing (b) of 2DPPV.



Fig.S12 Experimental (Red) compared with refined (Green) PXRD profiles of 2DPPVwith a serrated arrangement R_{wp} and R_p values converged to 3.40% and 7.12%, respectively.



Fig. S13. Calculation of pore size of2DPPV:a) snapshot of the simulated structure of serrated stacking modeand b) sketchdrawing of the configuration of layers along c axis, as taking the position of monomer M1 at (a) as a reference; c) and d)schematic pores(red and green ellipses)for the organization of type A and B; e)top view of pores (shadow areas) of the orthorhombic lattice; f) superposition of three figures (e) after in-plane rotation by60°, 0° , and +60°, the diameter of red circles represents the size of the pores.



Fig. S14 Unit cell (a) and eclipsed crystal lattice packing (b) of 2DPPV.



Fig. S15 Experimental (Red) compared with refined (Green) PXRD profiles of 2DPPVwith an eclipsed arrangement. R_{wp} and R_p values converged to 5.39% and 2.94%, respectively.



Fig. S16 Unit cell (a) and staggered crystal lattice packing (b) of 2DPPV.



Fig. S17 Experimental (Red) compared with refined (Green) PXRD profiles of 2DPPVwith a staggered arrangement. R_{wp} and R_p values converged to 11.79% and 19.98%, respectively



Fig. S19 Cyclic voltammetry curve of 2DPPV films in deaerated acetonitrile containing recrystallized nBu_4NPF_6 (0.1M) at room temperature (scan speed: 100 mVs⁻¹).



Fig. S20 a) Nitrogen adsorption-desorption isotherms and b) pore size distribution for 2DPPV-X (X=700, 800, 900 and 800a).



Fig. S21SEM images of (a) 2DPPV-700, (b) 2DPPV-800 and (c) 2DPPV-900.



Fig. S22N1s core level XPS spectra of (a) 2DPPV-700, (b) 2DPPV-800, (c) 2DPPV-900 and (d) 2DPPV-800a. The detailed weight contents of different nitrogen species were summarized in Table S7.



Fig. S23Galvanostatic charge/dischargecurves for 2DPPV-X (X=700, 800, 900) at different current densities in 6 M KOH electrolyte.



Fig. S24Capacitance retention for 2DPPV-800 in 6 M KOH.



Fig. S25 Ragone plot of the supercapacitor based on 2DPPV-800. We consider that the ultrathin graphitic layers with high electrical conductivity for carbon nanosheets, combing with highly porous features, can promote the ion and electron transport in the electrochemical process.

(<i>hk</i> 0)	$d_{\rm obs.}$ – spacing (nm)	$d_{\text{cal.}}$ – spacing (nm)			
(110)	3.14	3.14			
(020)	1.82	1.81			
(220)	1.59	1.56			
(040)	0.91	0.91			
(540)	0.74	0.74			
(640)	0.68	0.69			
(550)	0.62	0.63			
(060)	0.60	0.60			
(11 0 0)	0.57	0.57			
(12 0 0)	0.53	0.53			
(14 1 0)	0.45	0.45			
	<i>a</i> = 6.35 nm, <i>b</i> = 3.62 nm, <i>c</i> = 1.40 nm				

Table S1. Experimental and calculated *d*-spacings for hk0 reflections of the orthorhombic lattice of 2DPPV^(a).

^(a)Note: Only some of indexations are given in the table.

(<i>hk</i> 0)	$d_{\rm obs.}$ – spacing (nm)	$d_{\text{cal.}}$ – spacing (nm)			
(100)	3.14	3.14			
(110)	1.82	1.81			
(200)	1.59	1.56			
(220)	0.91	0.91			
(320)	0.74	0.72			
(410)	0.68	0.68			
(500)	0.62	0.63			
(330)	0.60	0.60			
(420)	0.00	0.59			
(510)	0.57	0.56			
(430)	0.52	0.52			
(600)	0.55	0.52			
(440)		0.45			
(530)	0.45	0.45			
(620)	0.45	0.44			
(700)		0.45			
$a_{\rm hex} = 3.62 \text{ nm}$					

Table S2. Experimental and calculated *d*-spacings for *hk*0 reflections of the hexagonalphase of 2DPPV.

		-					
	$S_{\rm BET}^{(a)}$	$S_{\text{Lang}}^{(b)}$	$S_{\rm micro}^{\rm (c)}$	$\underline{D}_{av}^{(d)}$	$V_{\rm micro}^{\rm (e)}$	$V_{\text{total}}^{(f)}$	$V_{\rm micro}/V_{\rm t}$
	$m^2 g^{-1}$	$m^2 g^{-1}$	$m^2 g^{-1}$	nm	cm ³ g ⁻¹	cm ³ g ⁻¹	ot
2DPPV	472	657	434	3.22	0.32	0.37	0.86

 Table S3. Nitrogen physisorption properties of 2DPPV.

Surface areas calculated from the N₂ adsorption isotherms using (a) BET and (b) Langmuir methods; (c) micropore surface area; (d) average pore size based on the adsorption isotherm; (e) micropore volume; (f) total pore volume at p/p0 = 0.99.

Table S4. HOMO, LUMO and optical band gaps of as-synthesized 2DPPV.

	LUMO	HOMO	OpticalBand gap
	/eV	/eV	/eV
2DPPV	-3.45	-5.55	2.10

Table S5. Nitrogen physisorption properties of 2DPPV-X (X=700, 800, 900 and 800a).

Sample	$S_{ m BET}{}^{[a]}$ (m ² g ⁻¹)	$S_{ m Lang}^{[b]}$ (m ² g ⁻¹)	$S_{ m micro}^{[c]}$ (cm ³ g ⁻¹)	$V_{tot}^{[d]}$ (cm ³ g ⁻¹)
2DPPV-700	529	662	374	0.26
2DPPV-800	304	451	164	0.16
2DPPV-900	258	383	148	0.15
2DPPV-800a	880	1102	655	0.40

Surface areas calculated from the N₂ adsorption isotherms using (a) BET and (b) Langmuir methods; (c) micropore surface area; (d) total pore volume at p/p0 = 0.99.

Sample	<i>N</i> (wt%)	Quternary N/ Pyridinic N		
2DPPV-700	1.36	59.2/40.8		
2DPPV-800	1.12	75.9/24.1		
2DPPV-900	1.04	77.3/22.7		
2DPPV-800a	0.82	63.5/36.5		

Table S6. Nitrogen contents of 2DPPV-X based on XPS analysis.

Samples	Electrolyte	Half-wave potential (V vs. RHE)	J @ 0.2V (mAcm ⁻²)	Literature
2DPPV-800a	0.1M KOH	0.67	-4.6	This work
Carbon nitride/graphene	0.1M KOH	0.69	-3.6	Angew. Chem. Int. Ed. 2011, 50, 5339
N-doped graphene quantum dots	0.1M KOH	0.65	-2.8	J. Am. Chem. Soc. 2012, 134, 15
N-doped ordered mesoporous carbon	0.1M KOH	0.69	-5.7	Angew. Chem. Int. Ed. 2010, 49, 2565
Macroporous C3N4/C	0.1M KOH	0.67	-5.0	Angew. Chem. Int. Ed. 2012, 51, 3892
Pt/C(Sigma-Aldrich)	0.1M KOH	0.8	-5.0	This work

 Table S7. ORR performance of as-prepared porous carbon nanosheet.

Table S8. Electrochemical capacitance of as-prepared porous carbon nanosheets.

Samples	Current density/ Ag ⁻¹	Electrolyte	$C_{ m g}$ /Fg ⁻¹	S _{ВЕТ} /m²g-1	Literature
2DPPV-700			181	529	
2DPPV-800	0.5	6М КОН	334	304	This work
2DPPV-900			262	258	
Aza-CMP@500	0.5	6М КОН	339	1227	Angew. Chem. Int. Ed. 2011 , 50, 8754
NMCSs-800	0.5	6M KOH	213	791	Adv. Mater.2014, 26, 3700
AC-SPN-3	0.5	6M KOH	214	1069	Sci. Rep. 2014 , 4, 5545
N-CNFs-900	0.5	6М КОН	230	562	ACS Nano 2012 , 6, 7092
pGSs-800	0.5	6M KOH	257	1834	Chem. Mater. 2014 , 26, 689
ТНРС	0.5	6М КОН	318	2870	Energy Environ. Sci. 2013, 6, 2497

Reference:

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