Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information

Rational bottom-up synthesis of sulphur-rich porous carbons for single-atomic platinum catalyst supports

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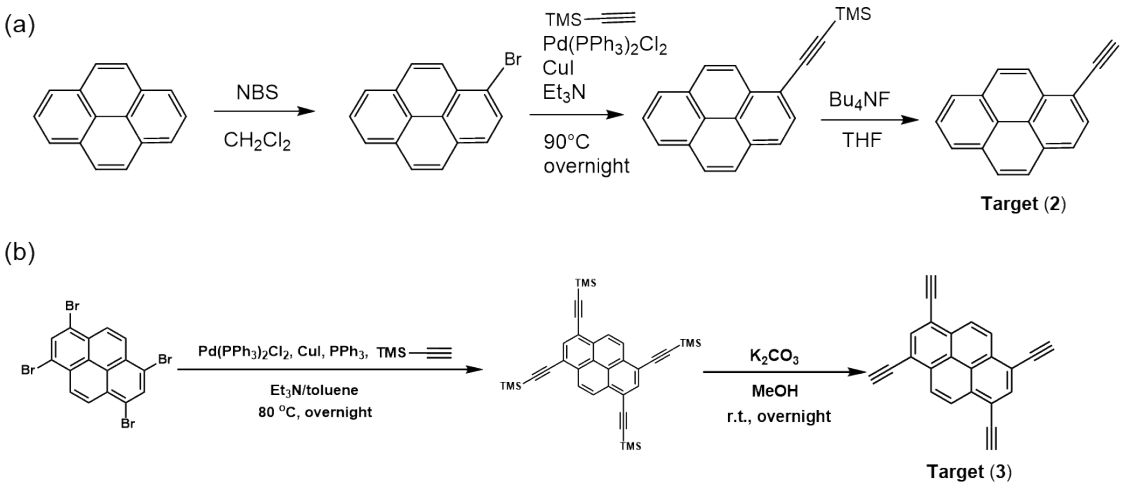
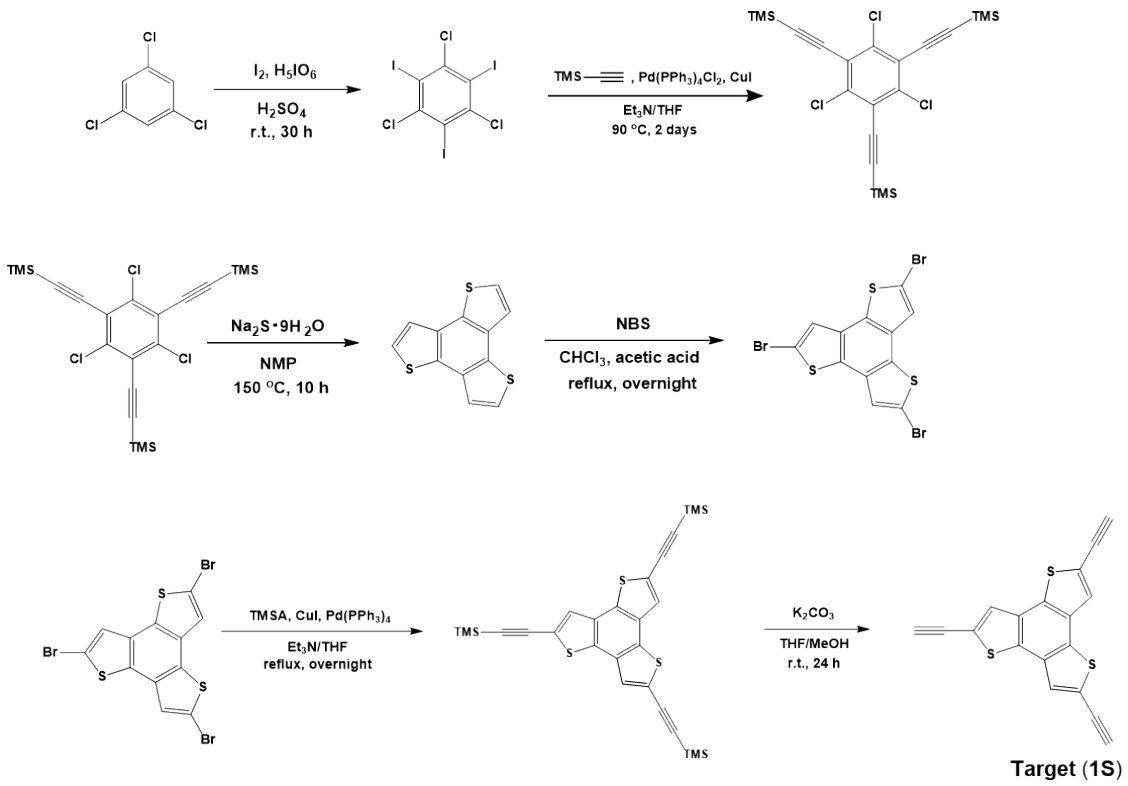


Scheme S1 Synthetic procedure of (a) 1-ethynylpyrene (**2**) and (b) 1,3,6,8-tetraethynylpyrrene (**3**).



Scheme S2 Synthetic procedure of 2,5,8-tri(triethynyl)benzo[1,2-*b*:3,4-*b*:5,6-*b*"]trithiophene (**1S**).

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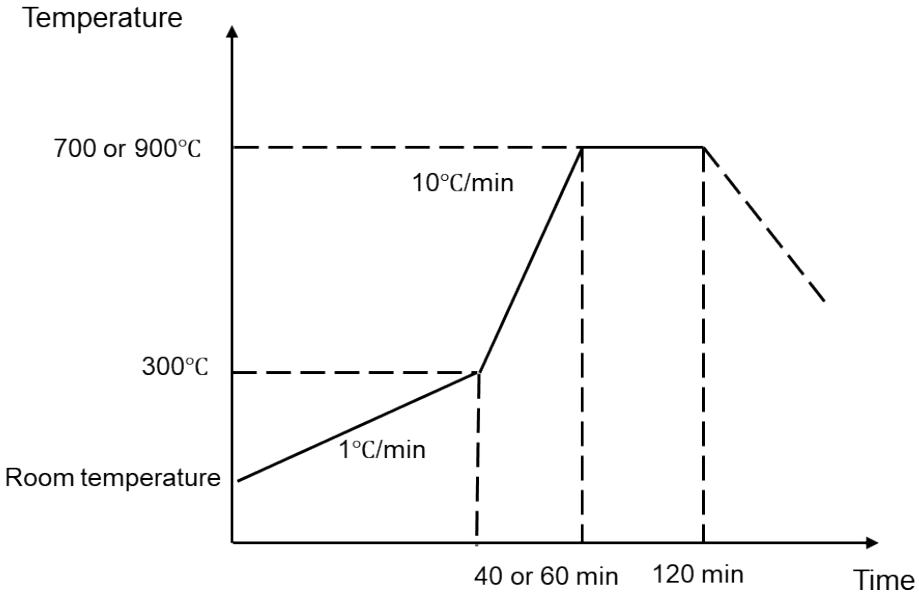

Scheme S3 Temperature profile for heat treatment.

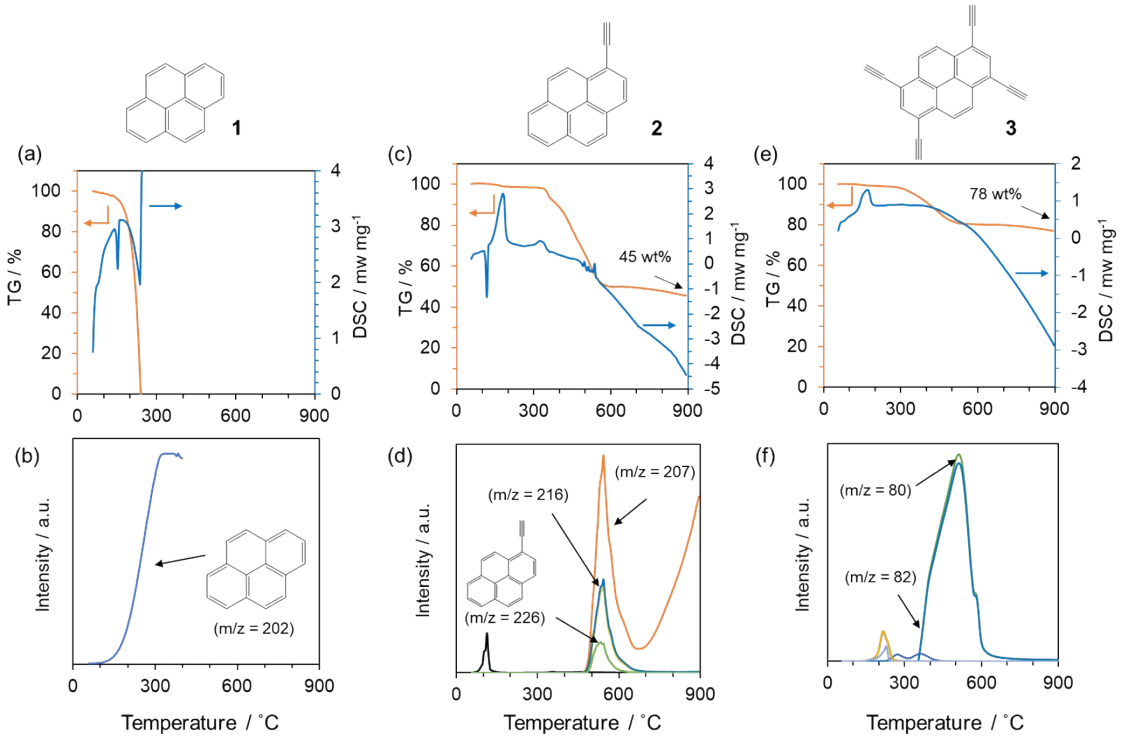

Fig. S1 TG-DSC profiles and the corresponding MS spectra of (a,b) **1**, (c,d) **2**, and (e,f) **3**.

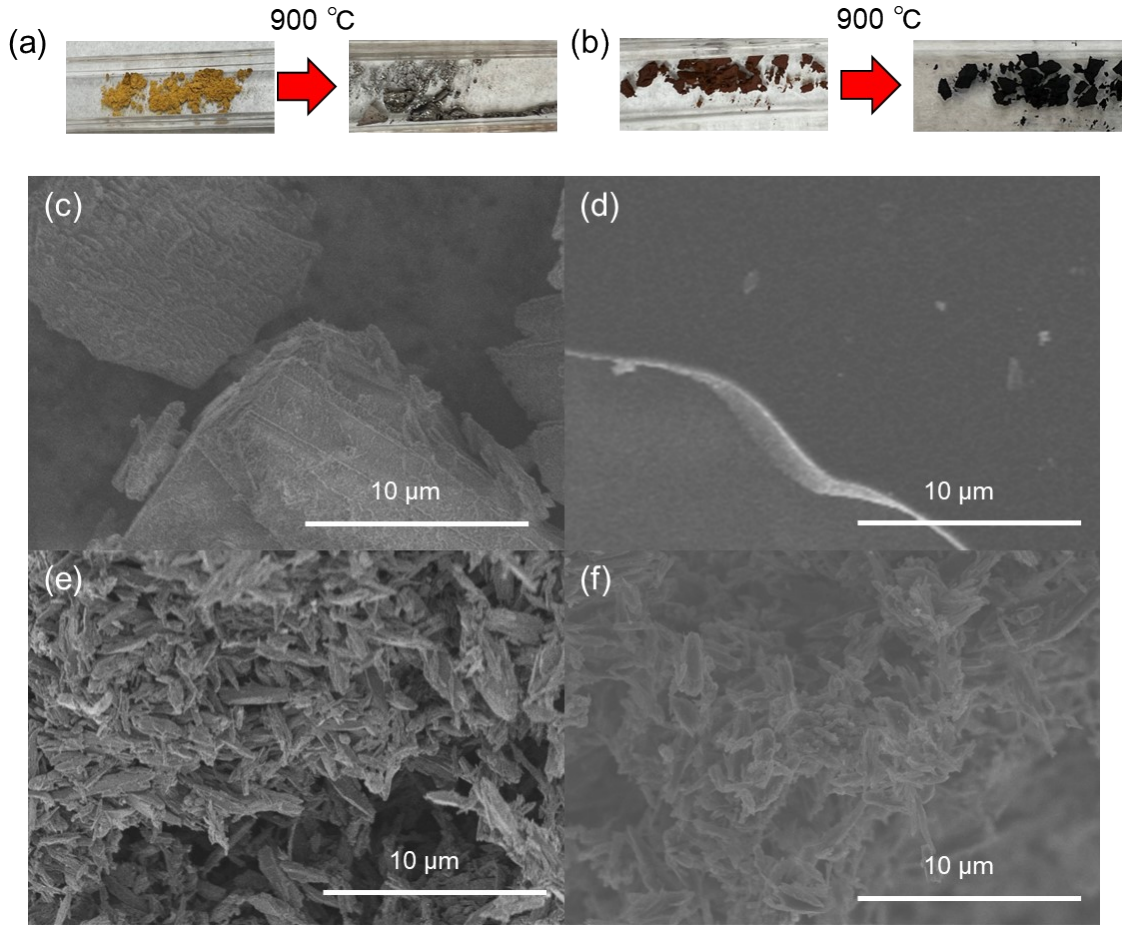

Fig. S2 Photos of (a) **2** and (b) **3** before and after heat treatment process at 900°C. SEM images of (c) **2**, (d) **2**_900, (e) **3**, and (f) **3**_900.

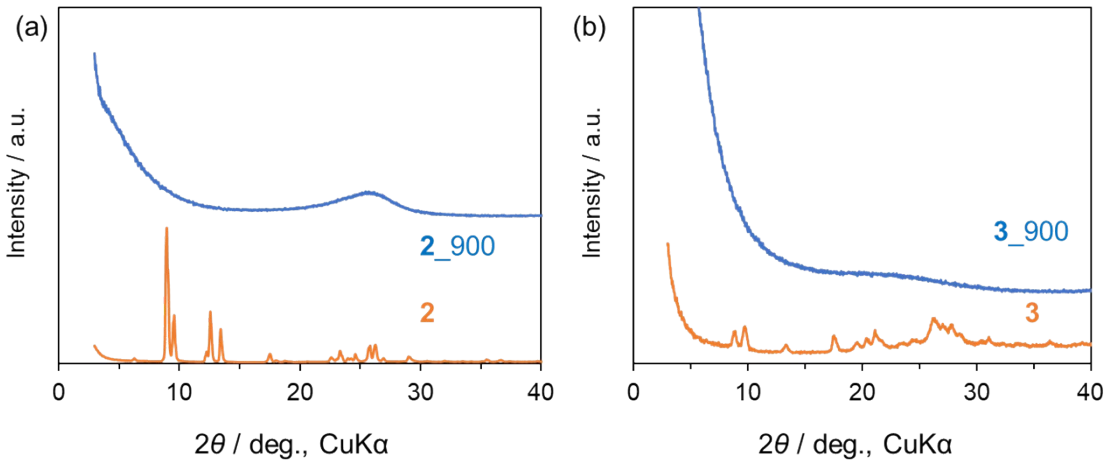

Fig. S3 PXRD patterns of (a) **2** and **2**_900, and (b) **3** and **3**_900.

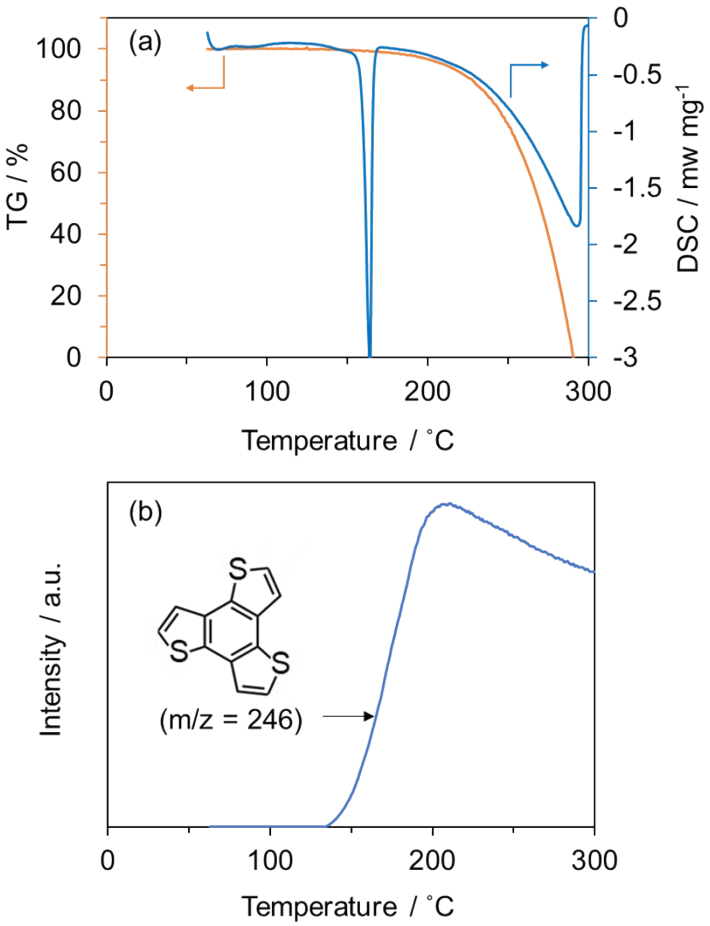

Fig. S4 (a) TG-DSC profiles and (b) the corresponding MS spectra of **2S**.

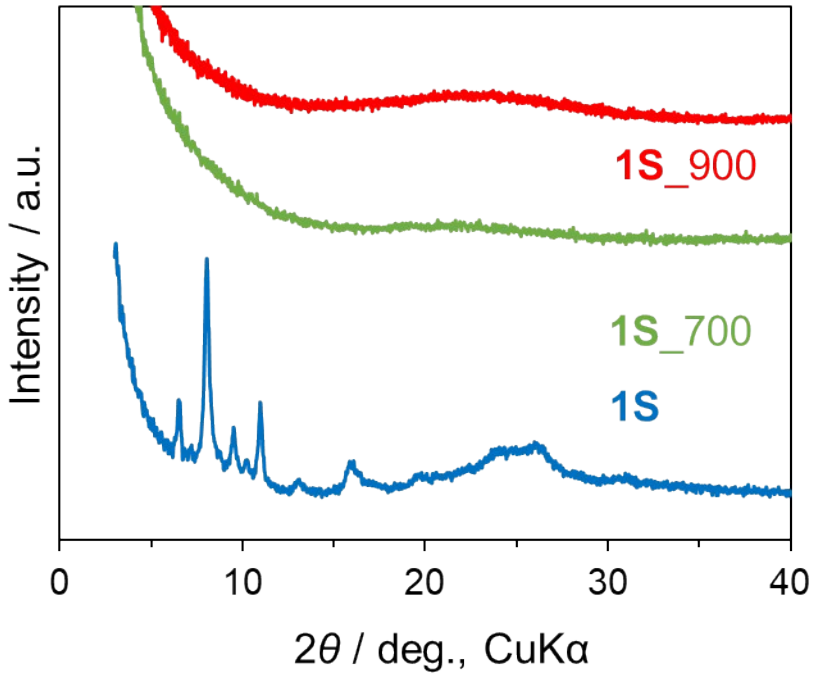

Fig. S5 PXRD patterns of of **1S**, **1S**_700, and **1S**_900 samples.

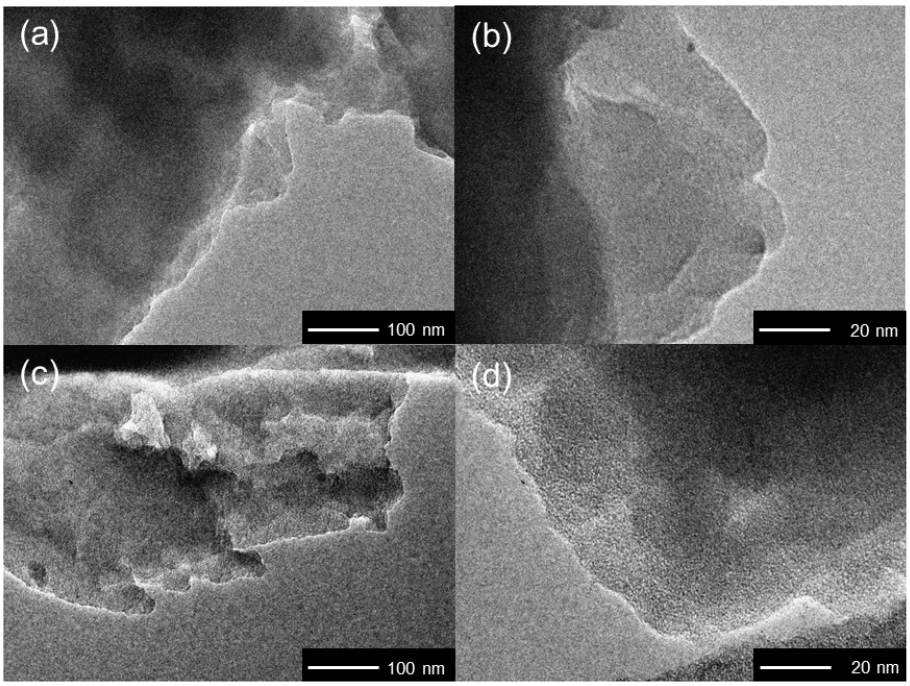

Fig. S6 TEM images of (a, b) **1S**_700 and (c, d) **1S**_900.

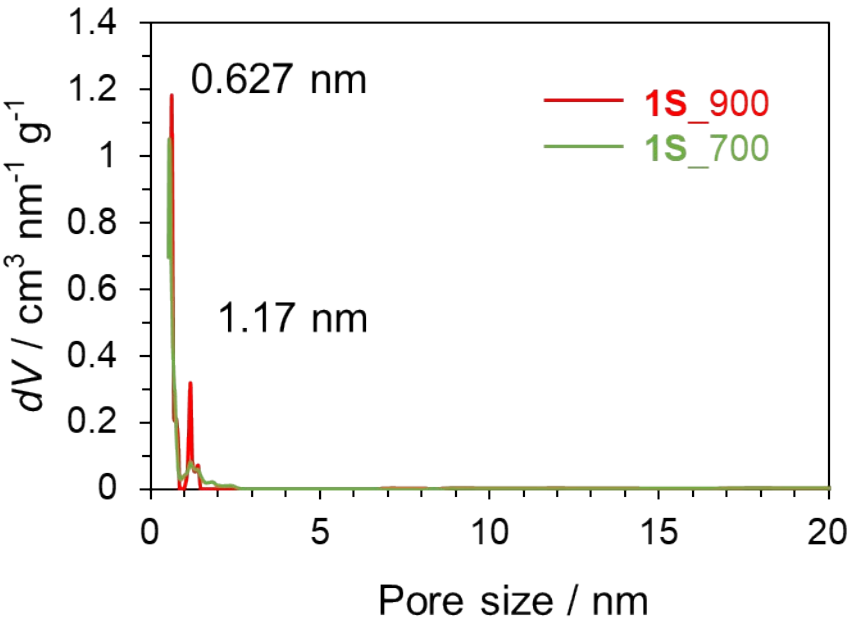

Fig. S7 Pore-size distributions of **1S**_700 and **1S**_900 calculated from the NLDFT method.

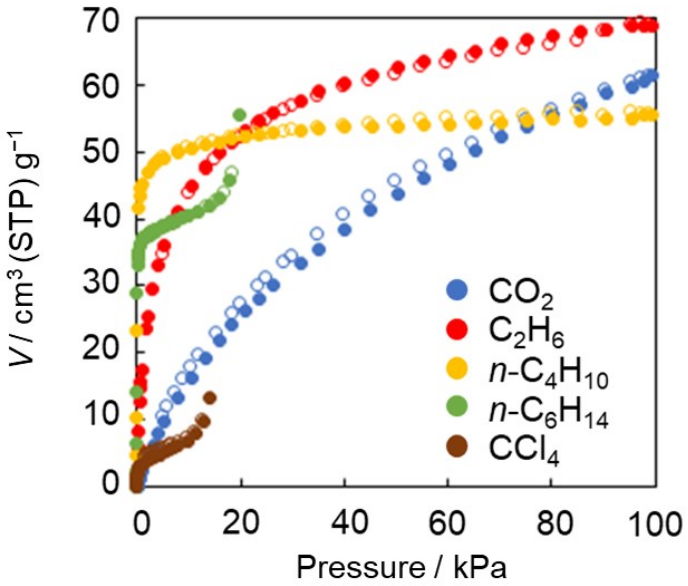

Fig. S8 CO_2 (25 ˚C, blue circle) ethane (25˚C, red circle), *n*-butane (25 ˚C, yellow circle), n-hexane (25 ˚C, green circle) and tetrachloromethane (25 ˚C, brown circle) adsorption/desorption isotherms of **1S**_900.

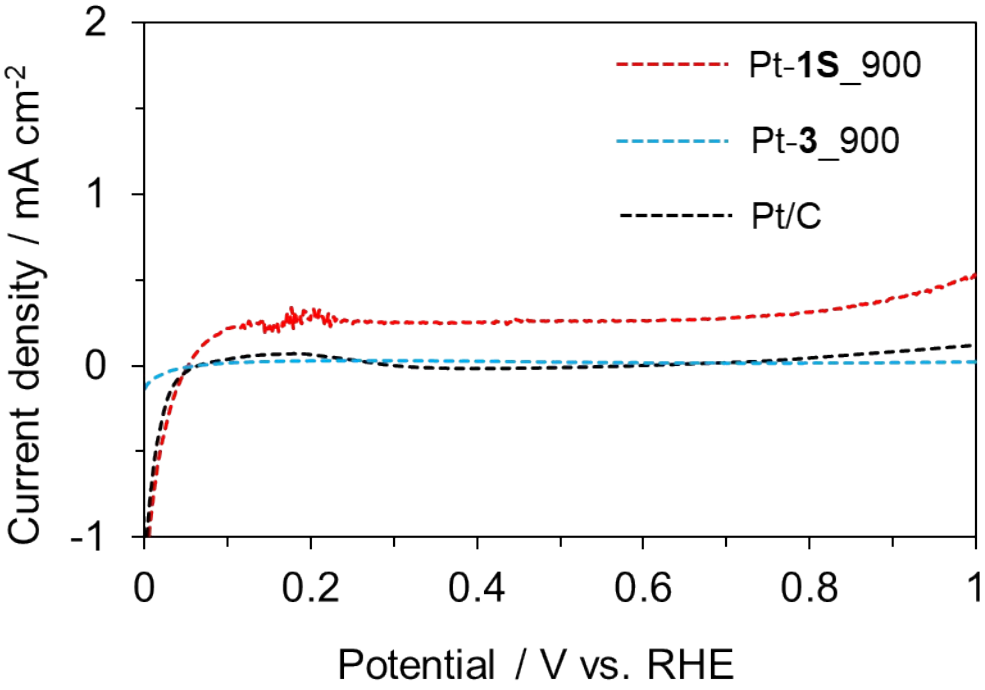

Fig. S9 Polarization curves of Pt-**1S**_900, Pt-**3**_900, and Pt/C under Ar flow.

Table S1 I_D/I_G ratio of carbonized **2**, **3** and **1S** samples.

Samples	I_D/I_G
2_900	0.92
3_900	1.0
1S_700	0.84
1S_900	0.98

Table S2 Elemental analysis results of carbonized **1S** samples**.**

Sample	C / wt %	S / wt %
1S_700	71.1	19.9
1S_900	84.4	15.6

Table S3 Porous textures of carbonized **1S**, **2** and **3** samples.

sample	S_{BET} / m^2 g^{-1}	V_{total}[α]/ cm^3 g^{-1}
1S	25	0.06
1S_700	714	0.31
1S_900	795	0.35
2	1	4.7×10^{-3}
2_900	0	1.3×10^{-5}
3	24	0.07
3_900	630	0.33

[α] The total pore volume was calculated at P/P_0 = 0.96.

Table S4 S contents and S_{BET} values of S-doped porous carbons reported in this work and previous works.

Entry	Temp. / °C	S content / wt%	S_{BET} / m^2 g^{-1}	Ref.
1	700	19.9	714	This work
2	900	15.6	796	This work
3	700	12.7	47	63
4	700	20.1	420	60
5	700	10.2	308	61
6	700	15.2	40	59
7	900	5.6	161	27
8	900	9.8	668	28
9	900	6.0	1189	62
10	900	2.9	1054	64
11	900	5.5	341	65
12	900	4.7	641	66
13	900	5.5	1292	67

Table S5 Pt content determined from Pt 4f XPS analysis for each catalyst before and after the LSV measurement.

Sample	Pt content / wt %	
	before	**after**
Pt-**1S**_900	0.68	0.75
Pt-**3**_900	0.12	-
Pt/C	8.60	8.52