

Supporting Information for

## **Bending Resistance Covalent Organic Framework Superlattice: “Nano-Hourglass”-Induced Charge Accumulation for Flexible In- Plane Micro-Supercapacitors**

Xiaoyang Xu<sup>1,3,#</sup>, Zhenni Zhang<sup>1,#</sup>, Rui Xiong<sup>1,#</sup>, Guandan Lu<sup>1</sup>, Jia Zhang<sup>1</sup>, Wang Ning<sup>1,3</sup>,  
Shuozhen Hu<sup>2,\*</sup>, Qingliang Feng<sup>3,\*</sup>, Shanlin Qiao<sup>1,4,\*</sup>

<sup>1</sup> College of Chemistry and Pharmaceutical Engineering, Hebei University of Science and  
Technology, Shijiazhuang, 050018, P. R. China

<sup>2</sup> State Key Laboratory of Chemical Engineering, East China University of Science and  
Technology, Shanghai 200237, P. R. China

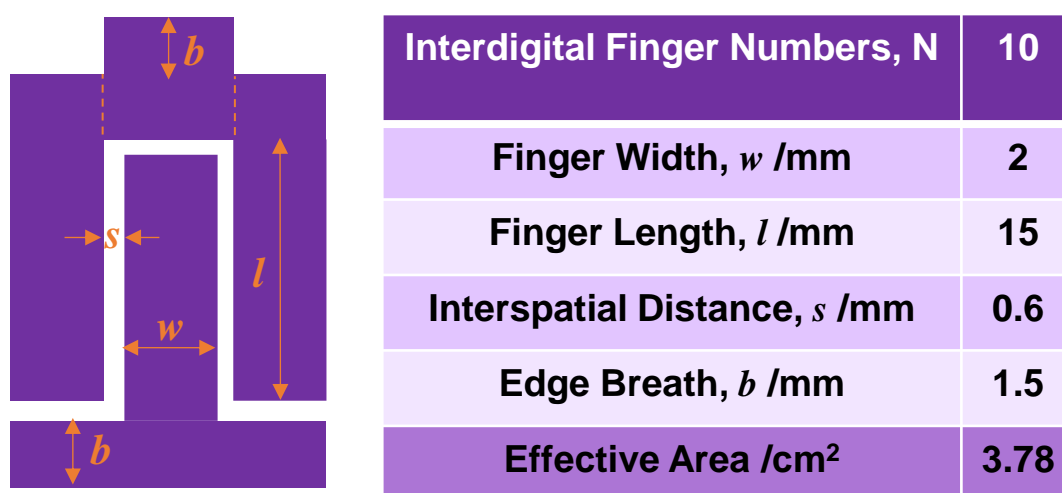
<sup>3</sup> School of Chemistry and Chemical Engineering, Northwestern Polytechnical University  
Xi'an 710072, P. R. China

<sup>4</sup> Hebei Electronic Organic Chemicals Engineering Center, Shijiazhuang 050018, P. R. China

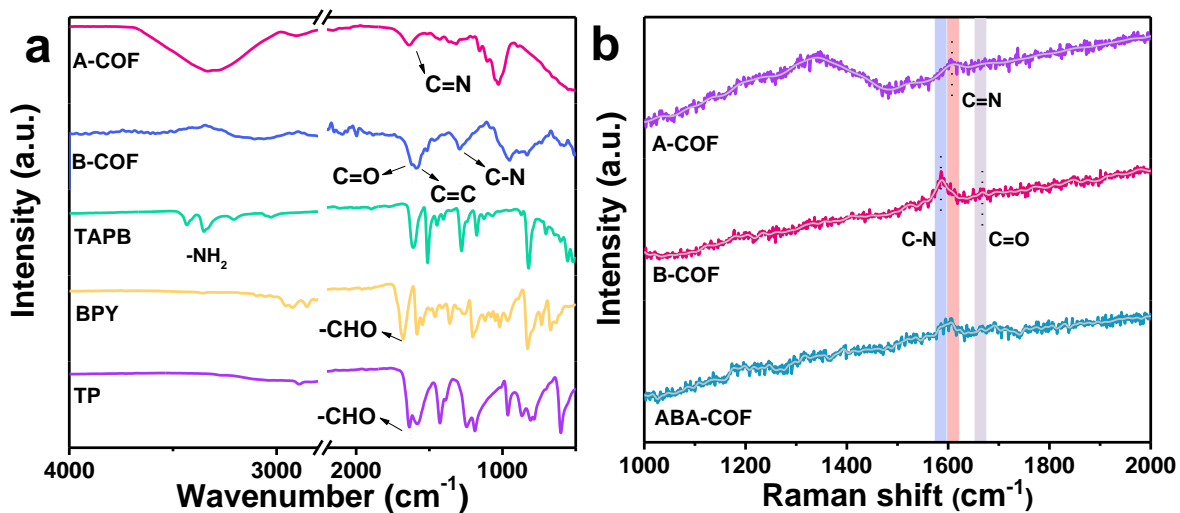
# Xiaoyang Xu, Zhenni Zhang, and Rui Xiong contributed equally to this work.

\* Corresponding authors. E-mail: [ccpeslqiao@hebust.edu.cn](mailto:ccpeslqiao@hebust.edu.cn) (S. Q.), [fengql@nwpu.edu.cn](mailto:fengql@nwpu.edu.cn)  
(Q. F.), [shuozhen.hu@ecust.edu.cn](mailto:shuozhen.hu@ecust.edu.cn) (S. H.)

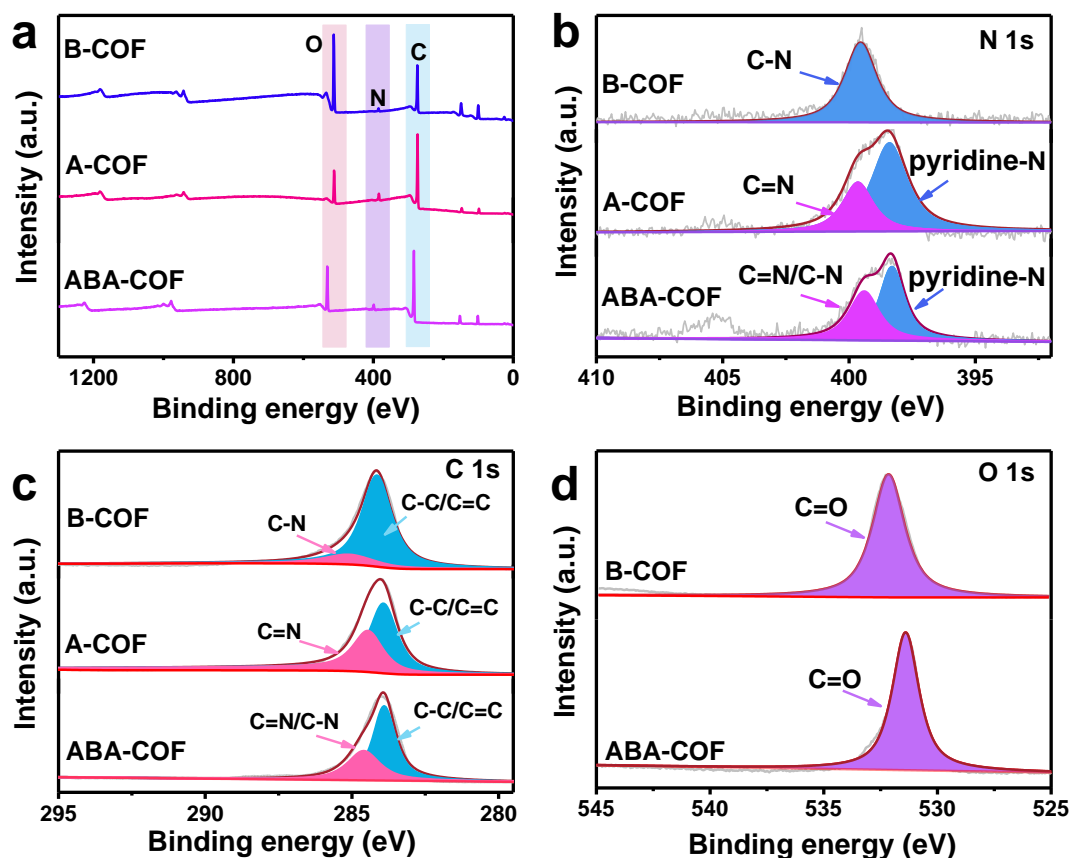
### **Supplementary Figures and Table**



**Fig. S1** The parameters of the prepared interdigitated electrodes with a custom-made interdigital mask



**Fig. S2** FT-IR spectra (a) of A- and B-COF films. Raman spectra (b) of A-COF, B-COF and ABA-COF superlattice films



**Fig. S3** XPS survey spectra (a), N 1s (b), and C 1s (c) of of A-COF, B-COF and ABA-COF superlattice films; O 1s (d) of B-COF and ABA-COF superlattice films

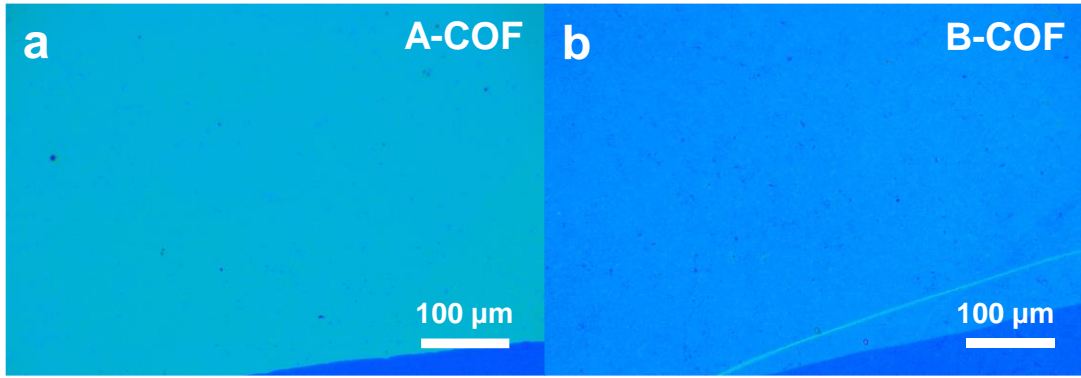


Fig. S4 OM images of A-COF (a) and B-COF (b) films

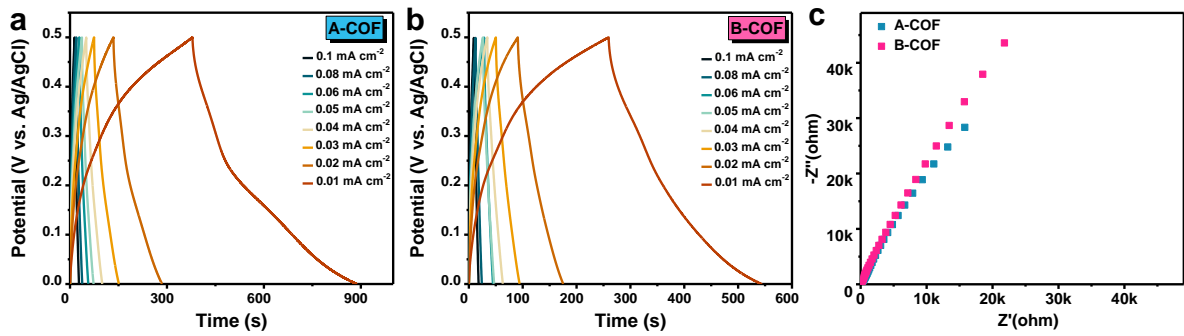


Fig. S5 GCD curves (a-b) and Nyquist plots (c) of A- and B-COF films

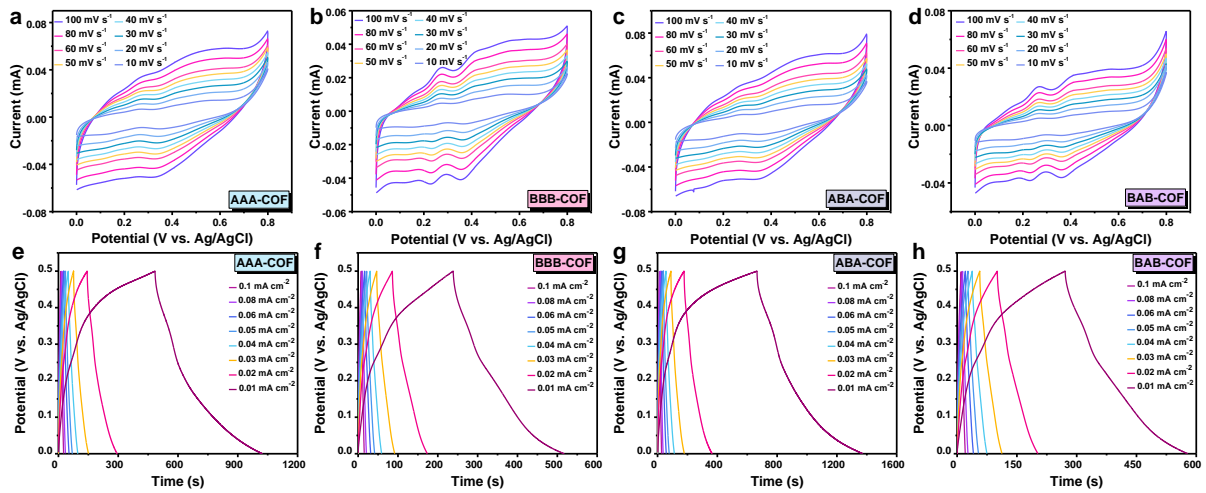
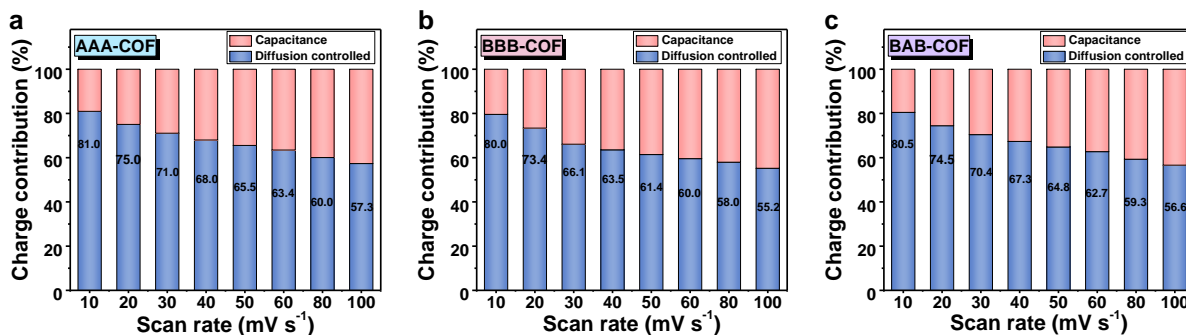
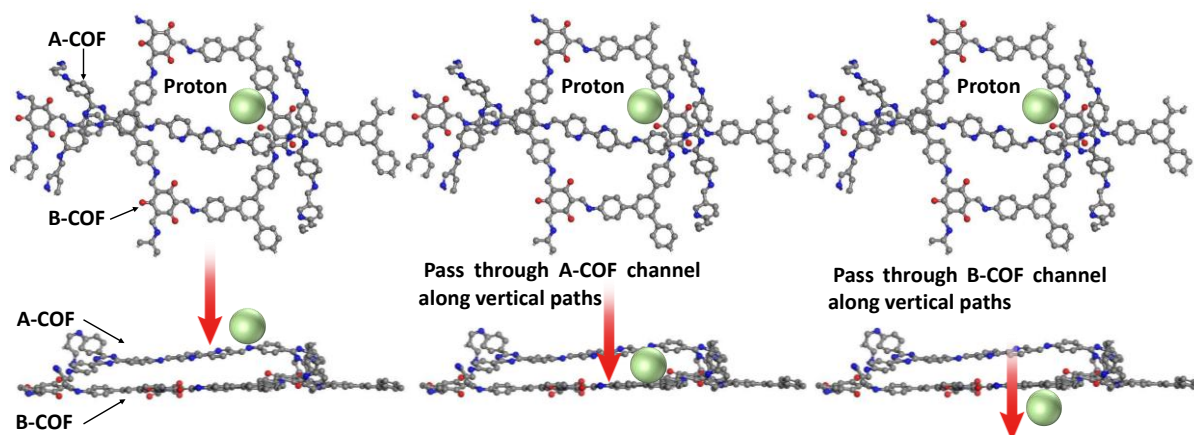


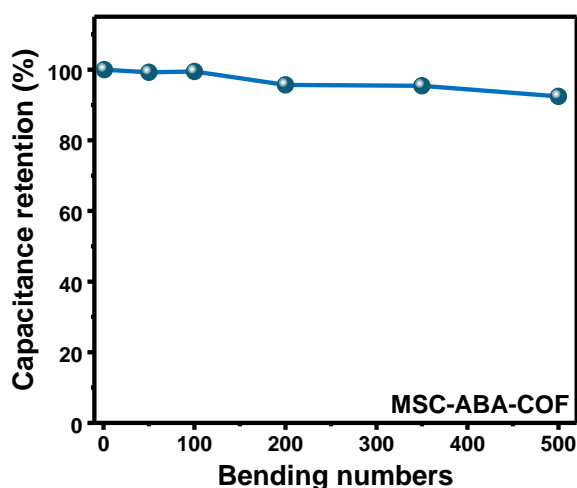
Fig. S6 CV (a-d) and GCD (e-h) of AAA-, BBB-, ABA- and BAB-COF superlattices



**Fig. S7** The diffusion-controlled and surface capacitance contribution of AAA-COF (a), BBB-COF (b) and BAB-COF (c) superlattices



**Fig. S8** The diagram of that proton passes through adjacent sites in the intine of A-COF and B-COF channel along vertical paths.



**Fig. S9** Capacitance retention of MSC-ABA-COF after repeat bending

**Table S1** The performance of recent reported 2D materials based MSCs and this work. <sup>(a)</sup> mV s<sup>-1</sup>; <sup>(b)</sup> mF cm<sup>-2</sup>; <sup>(c)</sup> F cm<sup>-3</sup>; <sup>(d)</sup> mWh cm<sup>-3</sup>; <sup>(e)</sup> W cm<sup>-3</sup>

Electrode	Electrolyte	Scan rate <sup>(a)</sup>	C <sub>A</sub> <sup>(b)</sup>	C <sub>V</sub> <sup>(c)</sup>	E <sub>v</sub> <sup>(d)</sup> (P <sub>v</sub> <sup>(e)</sup> )	Thickness	Capacitance retain	References
MPG	PVA/H <sub>2</sub> SO <sub>4</sub>	10	0.08	17.9	2.5 (495)	15 nm	98.3% after 100,000 cycles (50 V s <sup>-1</sup> )	Nat. Commun. 2013, 4, 2487.
PiCBA	PVA/H <sub>2</sub> SO <sub>4</sub>	50	0.171	34.1	4.7 (1323)	50.0 nm	86% after 350 cycles (50 mV s <sup>-1</sup> )	Angew. Chem. Int. Ed. 2017, 56 (14), 3920-3924.
EG/MXene	PVA/H <sub>3</sub> PO <sub>4</sub>	0.2 A/cm <sup>3</sup>	N <sub>A</sub>	184	3.4 (1.6)	2.5 μm	85.2% after 2,500 cycles (10 mV s <sup>-1</sup> )	Adv. Energy Mater. 2017, 7(4), 1601847.
MG-MSC	Ionogel electrolyte	10	0.338 (PVA/H <sub>2</sub> SO <sub>4</sub> )	197 (PVA/H <sub>2</sub> SO <sub>4</sub> )	23 (1860)	N <sub>A</sub>	96% after 20,000 cycles (100 V s <sup>-1</sup> )	Adv. Mater. 2018, 30(27), 1801384.
TaS <sub>2</sub>	PVA/LiCl	10	N <sub>A</sub>	508	58.5 (1.316)	330 nm	92% after 4,000 cycles (10 mV s <sup>-1</sup> )	J. Am. Chem. Soc. 2018, 140(1), 493-498.
g-C <sub>34</sub> N <sub>6</sub> -COF	PVA/LiCl	2	15.2	50.7	7.3 (0.05)	3 μm	93.1% after 5,000 cycles (10 mV s <sup>-1</sup> )	Angew. Chem. 2019, 58(35), 12065-12069.
PEDOT-CNT	PVA/H <sub>2</sub> SO <sub>4</sub>	10	20.6	82.4	11.4 (18.55)	2.5 μm	99.9% after 20,000 cycles (10 mV s <sup>-1</sup> )	Nanoscale 2019, 11 (16), 7761-7770.
IPNiO	SMPG-EGS	5	155	705	60 (70)	44.8 nm	≈90% after 8,000 cycles (10 mV s <sup>-1</sup> )	J. Mater. Chem. A 2019, 7 (37), 21496-21506.
g-C <sub>30</sub> N <sub>6</sub> -COF	EMIMBF <sub>4</sub> /PVDF-HFP	5	44.3	44.3	38.5 (0.3)	10 μm	95% after 5,000 cycles (10 mV s <sup>-1</sup> )	Sci. Bull. 2020, 65 (19), 1659-1666.
PbPPy	EMIMBF <sub>4</sub>	10	0.95	91.4	50.7 (1.83)	104 nm	85% after 10,000 cycles (10 mV s <sup>-1</sup> )	Adv. Funct. Mater. 2019, 30 (7), 1908243.
α-Co(OH) <sub>2</sub> /RGO	PVA/KOH	0.5 mA cm <sup>-2</sup>	130	260	20 (1.12)	11.6~13.5 nm	99.35% after 2,000 cycles (1 mA cm <sup>-2</sup> )	J. Colloid Interface Sci. 2021, 598, 1-13.
BCNN900	EMIMBF <sub>4</sub> /PVDF-HFP	0.25 mA cm <sup>-2</sup>	80.1	133.5	67.6 (0.8)	~6 μm	~91% after 10,000 cycles (10 mV s <sup>-1</sup> )	Energy Storage Mater. 2021, 42, 430-437.
rGO/GO film	(PVA)/H <sub>2</sub> SO <sub>4</sub>	0.25 mA cm <sup>-2</sup>	94.8	NA	10.7 (0.113)	120~200 nm	57.1% after 20,000 cycles (10 mV s <sup>-1</sup> )	Carbon 2021, 175, 27-35.

## Nano-Micro Letters

SPG-MSC	PVA/H <sub>3</sub> PO <sub>4</sub>	5	1.0	2	1.81 (297)	5 μm	91.8% after 10,000 cycles (0.2 mA cm <sup>-2</sup> )	Energy Environ. Sci. 2019, 12(5), 1534-1541.
MHCF/graphene	PVA/LiCl	5	19.8	93.2	44.6 (0.34)	~2 μm	96.8% after 5,000 cycles (10 mV s <sup>-1</sup> )	Mater. Horiz. 2019, 6(5), 1041-1049.
GEG	KTFSI-P14-TFSI	10	-	13.7	14.5 (5.19)	3 nm	93% after 10,000 cycles (10 μA cm <sup>-2</sup> )	Carbon 2022, 196, 203-212.
Cu-Ni-PPy	LiClO <sub>4</sub> /PVA	5	126.67	422	31.78 (0.15)	3 μm	89.3% after 10,000 cycles (50 mV s <sup>-1</sup> )	Energy Storage Mater. 2022, 51, 139-148.
GNRs	H <sub>2</sub> SO <sub>4</sub> /PVA	10	3.6	355	8 (550)	100 nm	93% after 10,000 cycles (1 V s <sup>-1</sup> )	Adv. Funct. Mater. 2022, 32 (16) 2109543
COE-4	H <sub>2</sub> SO <sub>4</sub> /PVA	0.04 mA cm <sup>-2</sup>	14.3	15.7	1.02 (2.37)	9.1±1.7 μm	87.3% after 5,000 cycles (50 mV s <sup>-1</sup> )	Energy Technol. 2022, 10 (5), 2200133
COF <sub>TAPB-DHPA</sub>	PVA/H <sub>3</sub> PO <sub>4</sub>	10	0.8	723.2	90.7 (2.3)	11.0 nm	97% after 5,000 cycles (1 V s <sup>-1</sup> )	Chem. Eng. J. 2022, 447, 137447.
IL-COF <sub>TAPB-DHPA</sub>			1.4	1157.9	139.7 (3.6)	11.7 nm	80% after 5,000 cycles (1 V s <sup>-1</sup> )	
Co-COF <sub>TAPB-DHPA</sub>			1.8	1790.1	230.4 (5.9)	10.0 nm	80% after 5,000 cycles (1 V s <sup>-1</sup> )	
<b>ABA-COF superlattice</b>	<b>PVA/H<sub>3</sub>PO<sub>4</sub></b>	<b>10</b>	<b>1.7</b>	<b>927.9</b>	<b>63.2 (3.3)</b>	<b>18.4 nm</b>	<b>83.9% after 8,000 cycles (80 mV s<sup>-1</sup>)</b>	<b>This work</b>