Supporting Information

Enhanced zinc reversibility enabled by zinc-bromide complexation of quasi-solid electrolyte for high-performance flexible zinc-air batteries

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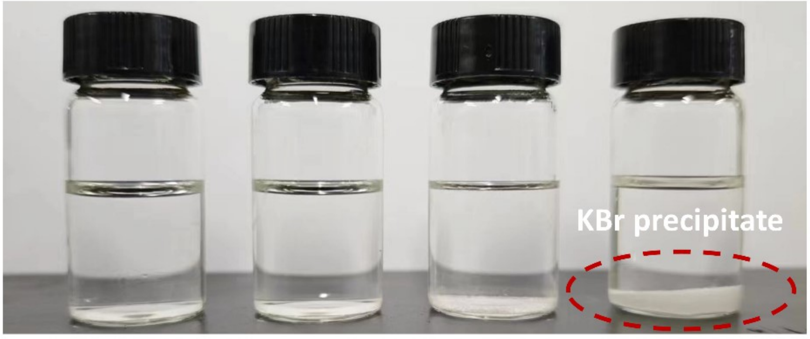
(a)



(b)

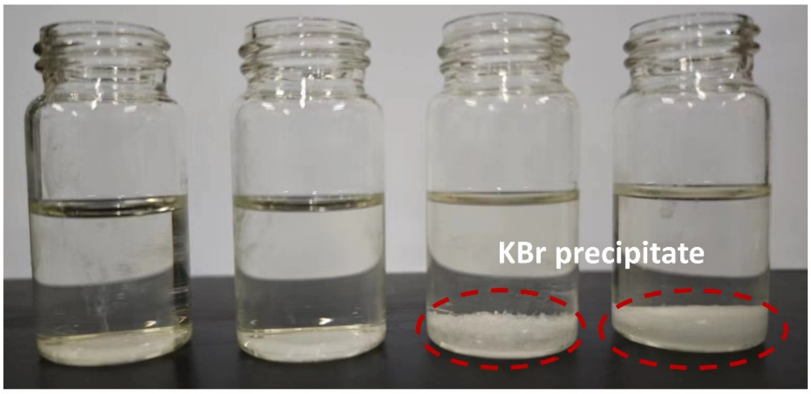


Figure S1. Optical images of solubility of 6 M KOH + 0.2 M $ZnAc_2$, 6 M KOH + 0.2 M $Zn(CH_3COO)_2$ + 1 M KBr, 6 M KOH + 0.2 M $Zn(CH_3COO)_2$ + 1.5 M KBr and 6 M KOH + 0.2 M $Zn(CH_3COO)_2$ + 2 M KBr (from left to right).

Different concentrations of KBr were added to 6 M KOH + 0.2 M $Zn(CH_3COO)_2$ to investigate its solubility. As shown in Figure S1a, the electrolyte is saturated with 1.5-2 M KBr. Theoretically, the higher content of KBr is favorable for the formation of more Zn-Br complexes. However, when the electrolytes were held in the ambient environment for 48 h, the KBr precipitates for the samples with 1.5 and 2 M KBr with the volatilization of water (Figure S1b). Considering the inevitable water loss of QSEs in the half-open structure of FZABs, the precipitation of KBr in the saturated electrolyte probably happens, diminishing the interfacial stability between the electrolyte and electrode. Therefore, the addition of 1 M KBr was chosen.

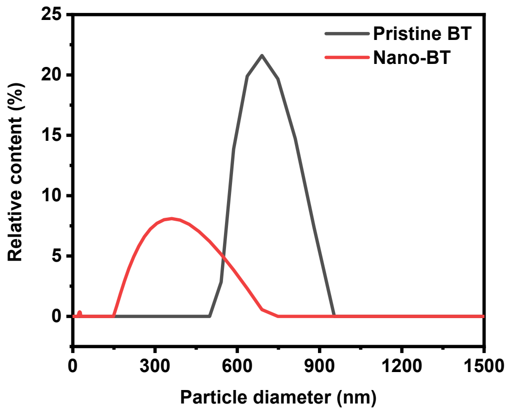


Figure S2. The particle size distribution curves of nano-BT and pristine BT.

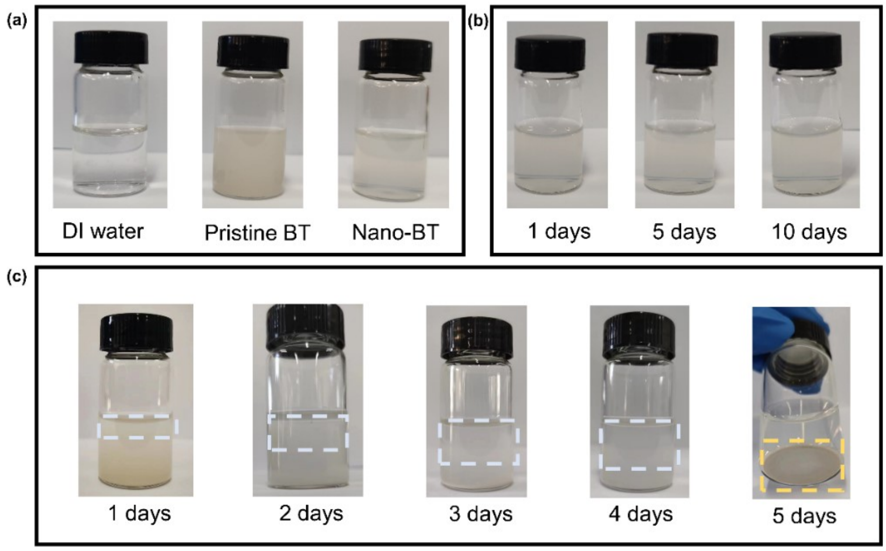


Figure S3. (a) Optical images of DI water, pristine BT and nano-BT. Optical images of (b) nano-BT with a standing time of 1, 5 and 10 days, and (c) pristine BT with a standing time of 1, 2, 3, 4 and 5 days, respectively.

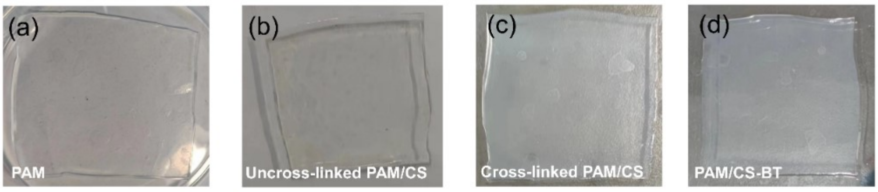
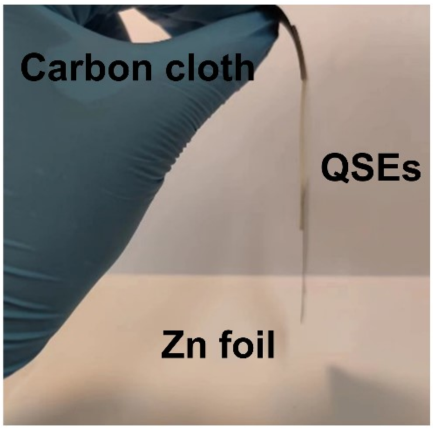


Figure S4. Optical images of (a) PAM hydrogel, (b) uncross-linked PAM/CS hydrogel, (c) cross-linked PAM/CS hydrogel, and (d) PAM/CS-BT hydrogel.



Electrode adhesion

Figure S5. Optical image of adhesion of PAM/CS-BT to Zn and air electrodes.

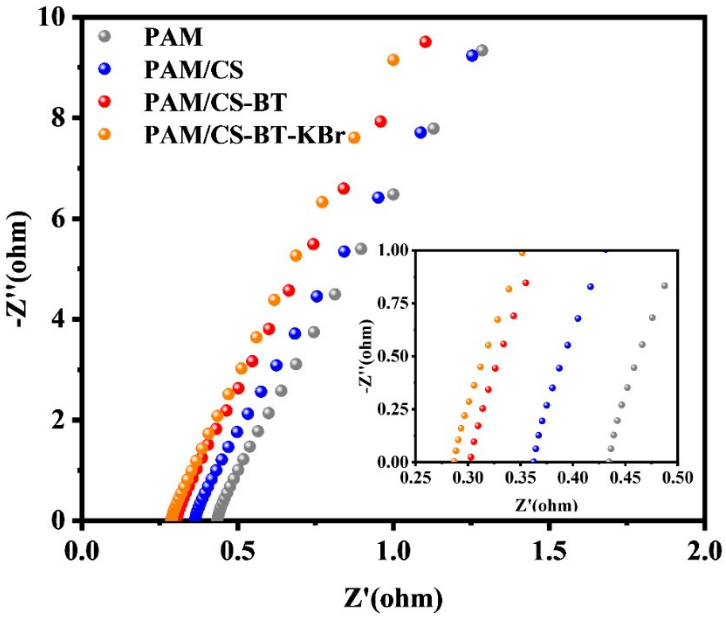


Figure S6. AC impedance diagram of different QSEs tested after sufficient electrolyte swelling.

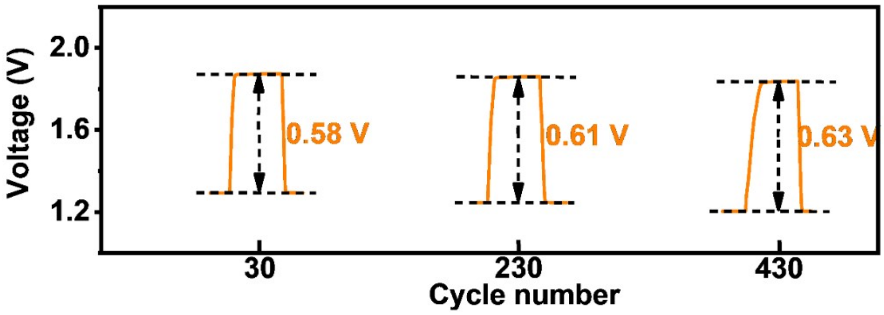


Figure S7. Voltage hysteresis cycle test of FZABs with PAM/CS-BT-KBr QSEs at 2 mA cm^{-2}.

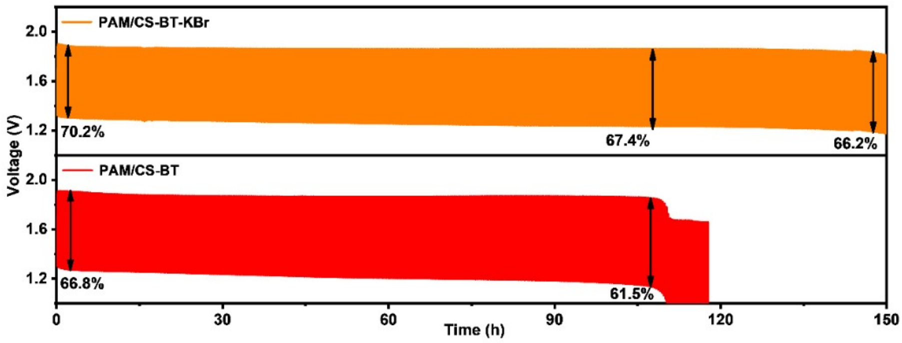


Figure S8. Galvanostatic discharge/charge curves of FZABs with PAM/CS-BT and PAM/CS-BT-KBr QSEs at 2 mA cm^{-2}.

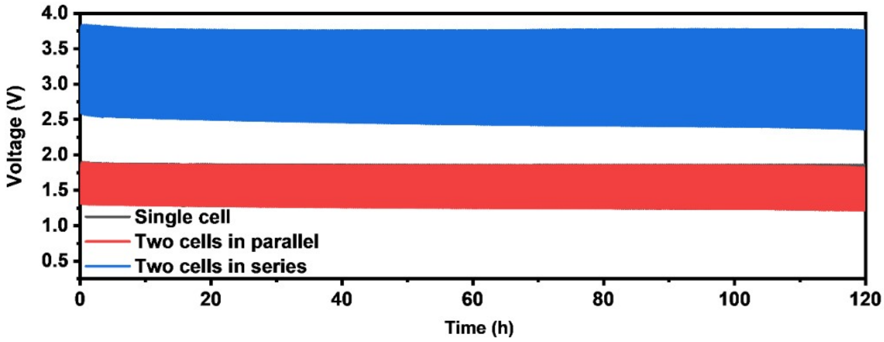


Figure S9. Galvanostatic discharge/charge curves of one cell, two cells in series and two cells in parallel with PAM/CS-BT-KBr QSEs at 2 mA cm^{-2}.

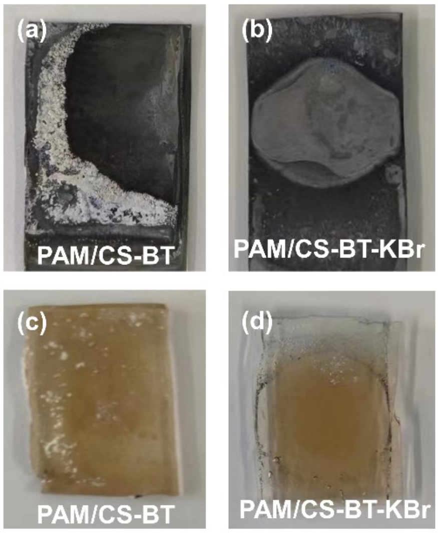


Figure S10. (a, b) Optical images of cycled Zn anodes from PAM/CS-BT-based and PAM/CS-BT-KBr-based FZABs, respectively. (c, d) Optical images of cycled PAM/CS-BT and PAM/CS-BT-KBr electrolytes.

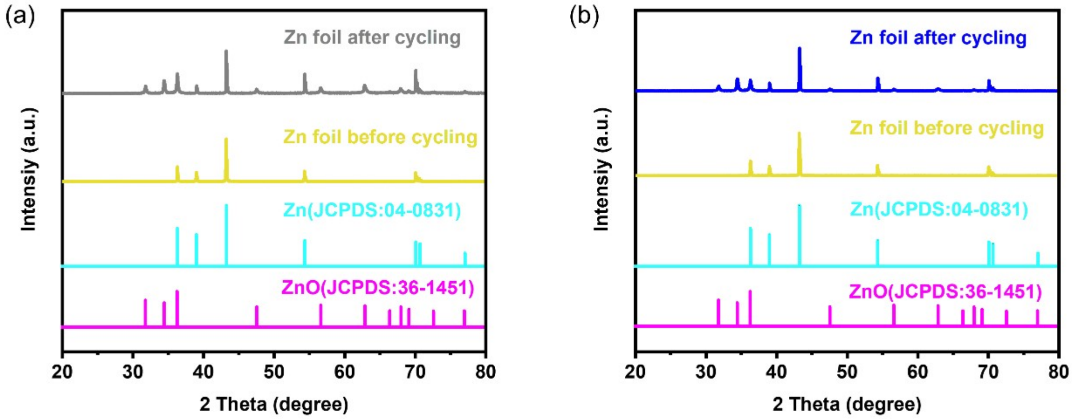


Figure S11. XRD patterns of the initial and cycled Zn anodes using (a) PAM and (b) PAM/CS electrolytes.

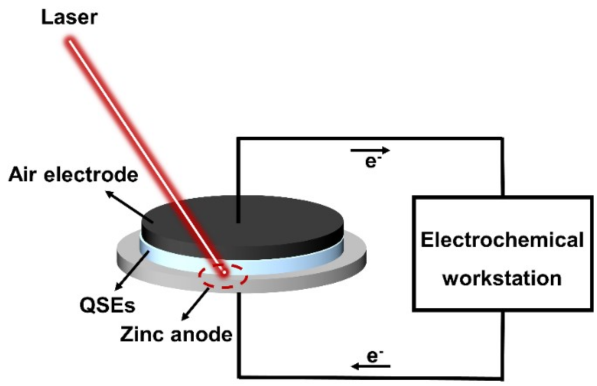


Figure S12. Schematic diagram of in-situ Raman spectroscopy testing.

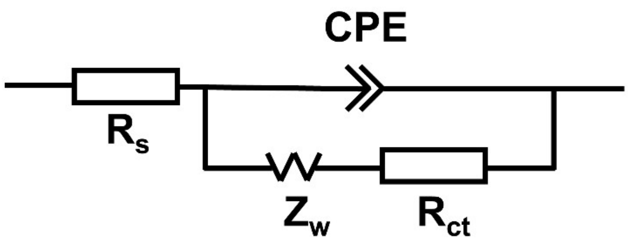


Figure S13. The equivalent circuit used to fit the Nyquist plots.

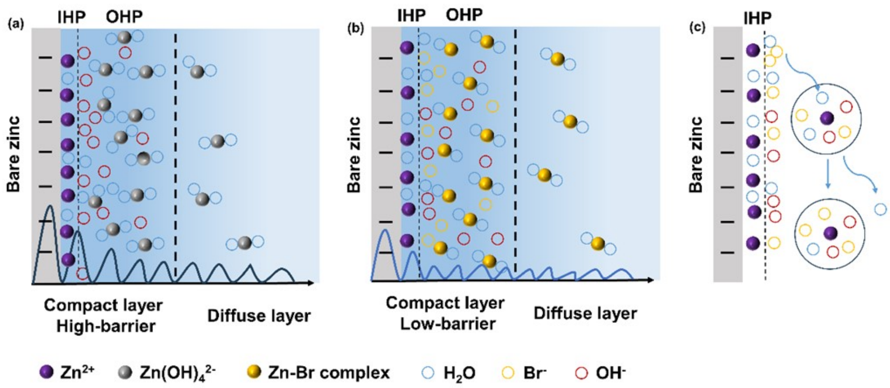


Figure S14. Electric double layer structure in the vicinity of anode and the corresponding energy barrier of (a) PAM/CS-BT and (b,c) PAM/CS-BT-KBr electrolytes.

Table S1. Comparative summary of open-circuit voltage and power density of PAM/CS-BT-KBr-based FZABs in this work and other reported studies on QSEs.

Electrolyte	Catalyst	Open-circuit voltage (V)	Power density (mW cm^{-2})	Ref
PAM/CS-BT-KBr	Pt/C+RuO_2 (0.5 mg cm^{-2})	1.48	153.3	This work
PVA-0.075TMG 3 M KOH	Co_3O_4/carbon paper	1.3	84.1	1
PAA 30 wt% KOH	Pt/C+RuO_2	/	~120	2
	BFC-FC-0.2	1.49	160	
PVAA-cellulose 6 M KOH	CoFeP@C (1 mg cm^{-2})	1.41	74	3
BC-4 M KOH-2 M KI	Pt/C+RuO_2	1.34	129	4
PAMPS-K25-MC2.0-5M	Co_3O_4/carbon black	~1.35	73.9	5
PAMNa-CMCS 6 M KOH	Pt/C+RuO_2 (2 mg cm^{-2})	1.4	120.87	6
PAM-PAA-6 M KOH	Pt/C+RuO_2 (1 mg cm^{-2})	1.42	11.8	7
PANa-St	Pt/C+RuO_2 (2 mg cm^{-2})	1.40	67.5	8
PU-PES-fiber 6 M KOH	/	1.4	68.7	9
HP-PVA/PAA 6 M KOH	Pt/C+RuO_2 (0.4 mg cm^{-2})	1.415	70.5	10
PAM-CNF/KOH/KI	Pt/C+RuO_2 (2 mg cm^{-2})	1.4	~63	11
PAAK-M	/	/	126	12
PAM-F/G	/	1.4	155	13
PAM-SA/PhCs	Mn-Co-Fe@CNT	1.45	87	14
M-Agar-6 M KOH	Mn-Co-Fe@CNT/nickel foam	1.46	126	15
C-HGE0.5	Co_3O_4/CNTs	/	62.2	16
AEPEM-GF 6 M KOH	Pt/C+RuO_2	1.45	140	17
TEAOH-KOH/PVA	Co_3O_4/LIG	1.39	/	18
CNF-FHE(PANa/CNF)	FeCo-ONS (2.5 mg cm^{-2})	1.49	30	19
MXene/Zn-LDH-array@PVA	Pt/C+RuO_2 (0.5 mg cm^{-2})	1.37	92.3	20
PAMPS/PAM/DMSO	Co_3O_4/RuO_2 (0.2 mg cm^{-2})	/	56.8	21
Agar-PVA/GO DN	/	/	123.7	22

6 M KOH				
Starch gel-KOH	Mn-Co-Fe@CNT	1.43	84	23
PAM/SA/KI	Pt/C+RuO_2 (1 mg cm^{-2})	1.43	132	24
PANa/CNF	Co-N-Cs (1 mg cm^{-2})	/	128	25
HPPAN	CoN-CS (1 mg cm^{-2})	1.46	123.8	26
ANF-PVA	Co/CNT (0.4 mg cm^{-2})	~1.5	67.5	27
HAcc@HPPAN-COONa/PANa	Pt/C+RuO_2 (0.5 mg cm^{-2})	1.45	126	28
PAM-SC	CoFe/AC	1.37	107.64	29

Table S2. Comparative summary of lifespan of PAM/CS-BT-KBr-based FZABs in this work and other reported studies on QSEs.

Electrolyte	Catalyst	Current Density (mA cm^{-2})	Lifespan	Ref
PAM/CS-BT-KBr	Pt/C+RuO_2 (0.5 mg cm^{-2})	2	150 h 450 cycles	This work
PVA-0.075TMG 3 M KOH	Co_3O_4/carbon paper	5	16 h 100 cycles	1
PAA 30 wt% KOH	Pt/C+RuO_2	2	40 h 180 cycles	2
	BFC-FC-0.2		105 h 600 cycles	
PVAA-cellulose 6 M KOH	CoFeP@C (1 mg cm^{-2})	3	54 h 324 cycles	3
BC-4 M KOH-2 M KI	Pt/C+RuO_2	/	17 h 100 cycles	4
PAMPS-K25-MC2.0-5M	Co_3O_4/carbon black	1	70 h 210 cycles	5
PAMNa-CMCS 6 M KOH	Pt/C+RuO_2 (2 mg cm^{-2})	5	86 h	6
PAM-PAA-6 M KOH	Pt/C+RuO_2 (1 mg cm^{-2})	1	10 h 100 cycles	7
PANa-St	Pt/C+RuO_2 (2 mg cm^{-2})	/	44 h 132 cycles	8
PU-PES-fiber 6 M KOH	/	1	5 h 30 cycles	9
HP-PVA/PAA 6 M KOH	Pt/C+RuO_2 (0.4 mg cm^{-2})	1	189 cycles	10
PAM-CNF/KOH/KI	Pt/C+RuO_2 (2 mg cm^{-2})	2	75 h 225 cycles	11
PAAK-M	/	2	55 h	12
PAM-F/G	/	2	40 h	13
PAM-SA/PhCs	Mn-Co-Fe@CNT	2	30 h 180 cycles	14
M-Agar-6 M KOH	Mn-Co-Fe@CNT/nickel foam	2	25 h 75 cycles	15
C-HGE0.5	Co_3O_4/CNTs	3	60 h 180 cycles	16
AEPEM-GF 6 M KOH	Pt/C+RuO_2	5	28 h 168 cycles	17
TEAOH-KOH/PVA	Co_3O_4/LIG	0.5	20 h 133 cycles	18
CNF-FHE(PANa/CNF)	FeCo-ONS	1	85 h	19

	(2.5 mg cm^{-2})			
MXene/Zn-LDH-array@PVA	Pt/C+RuO_2 (0.5 mg cm^{-2})	3	50 h 100 cycles	20
PAMPS/PAM/DMSO	Co_3O_4/RuO_2 (0.2 mg cm^{-2})	1	59 h 177 cycles	21
Agar-PVA/GO DN 6 M KOH	/	0.5	64 h 384 cycles	22
Starch gel-KOH	Mn-Co-Fe@CNT	2	36 h 200 cycles	23
PAM/SA/KI	Pt/C+ RuO_2 (1 mg cm^{-2})	1	110 h 330 cycles	24
PANa/CNF	Co-N-Cs (1 mg cm^{-2})	2	110 h	25
HPPAN	CoN-CS (1 mg cm^{-2})	3	54 h 162 cycles	26
ANF-PVA	Co/CNT (0.4 mg cm^{-2})	1	118 h 355 cycles	27
HAcc@HPPAN-COONa/PANa	Pt/C+RuO_2 (0.5 mg cm^{-2})	2	100 h 300 cycles	28
PAM-SC	CoFe/AC	0.5	42 h 420 cycles	29

Table S3. Fitted charge transfer resistance (R_{ct}) of FZABs with PAM/CS-BT and PAM/CS-BT-KBr electrolytes at different temperatures.

	PAM/CS-BT		PAM/CS-BT-KBr	
Temperature (℃)	R_{ct} (Ω)	Relative standard errors (%)	R_{ct} (Ω)	Relative standard errors (%)
5	18.87	6.59	7.43	3.95
10	16.66	7.88	6.41	4.62
15	14.36	7.67	5.71	5.54
20	12.06	7.99	5.00	6.10
25	10.18	8.52	4.55	7.65

Supplementary References

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