Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Power Output and Carrier Dynamic Studies of Perovskite Solar Cells under Working Conditions

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S1. Characterization of the perovskite films

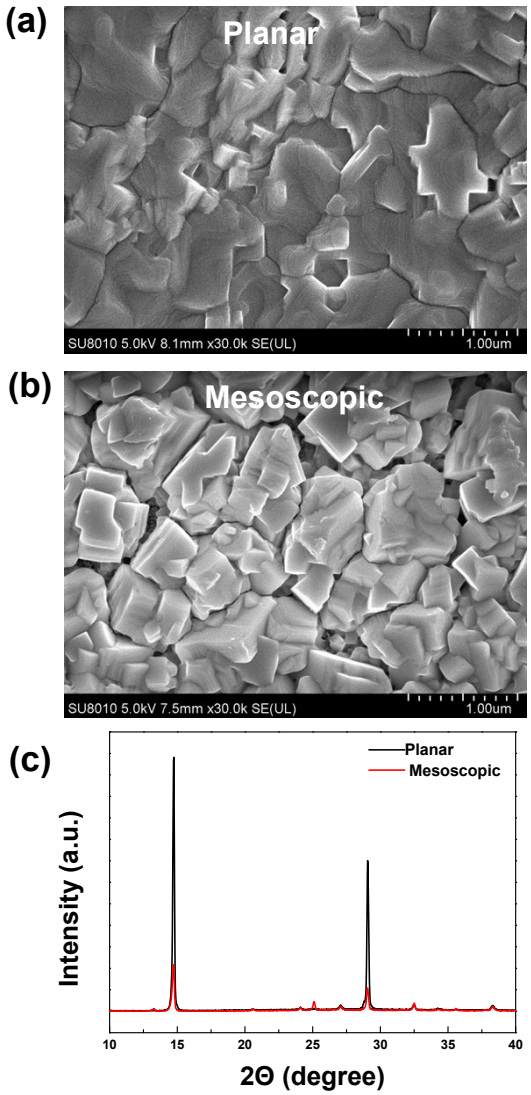


Fig. S1 SEM images of perovskite films for (a) planar and (b) mesoscopic devices; (c) the corresponding XRD patterns of two targeted samples.

S2. Device characterization

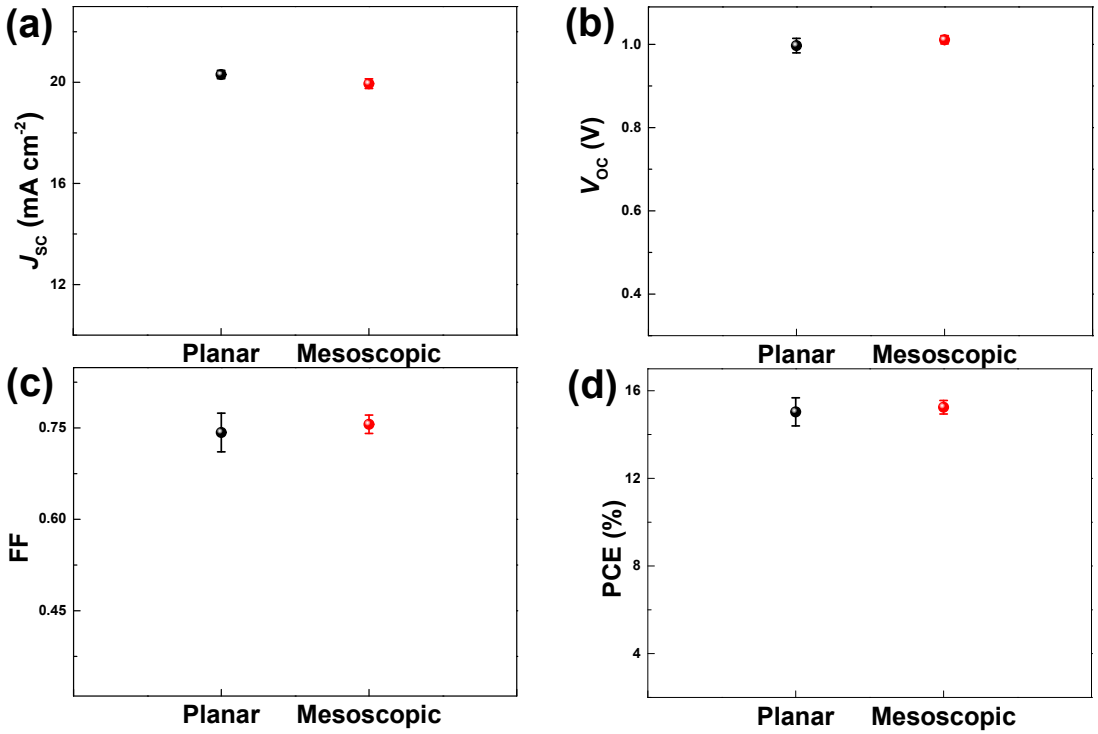


Fig. S2 The statistical photovoltaic parameters (a: J_{SC}, b: V_{OC}, c: FF and d: PCE) of the planar and mesoscopic perovskite solar cells.

S3. The equivalent circuit of working conditions and the detailed theoretical deduction of the power output

The solar cell can act as the power source in a simple electric circuit and the equivalent circuit is shown in Fig. S3a. According to the Ohm's law, the equivalent resistance of external circuit can be calculated as $R_E = Rr/(R+r)$, where R is the input impedance of the digital oscilloscope (1 MΩ), r is the controlled loads from the variable resistor. Based on the voltage and the resistance obtained from the equivalent circuit, the current density can be determined by $J = V_{work}/SR_E$, where S is the effective area of LED spot (2 mm×2 mm). The J-V curves of the planar and mesoscopic devices in the equivalent circuits under various light intensities are shown in Fig. S3b and Fig. S3c.

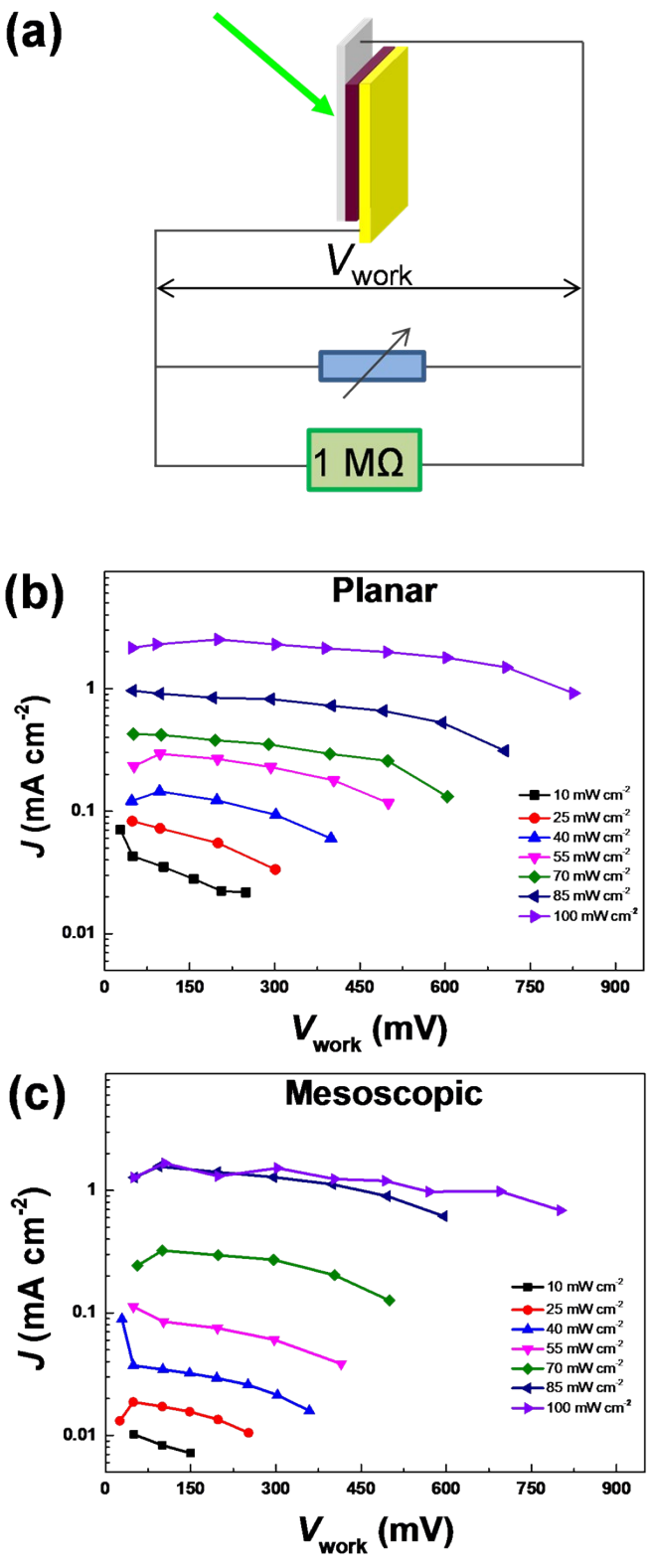


Fig. S3 (a) Equivalent circuit of the simulated working condition. *J-V* curves for (b) planar and (c) mesoscopic perovskite solar cells under working conditions.

S4. The fitting results of TPV, TPC and TVVD

Table S1 Parameters of bi-exponential fitting for TPV decay trace (planar perovskite solar cell).

V_{ph} (mV)	A_1	τ_1 (s)	A_2	τ_1 (s)	τ (s)
29	0.75417	0.00343	0.25583	0.01066	0.00526
53	0.74041	0.00162	0.25659	0.01044	0.00389
80	0.69536	0.00122	0.32464	0.01169	0.00455
107	0.75721	9.20E-04	0.31794	0.00688	0.00268
133	0.63862	9.64E-04	0.36138	0.00494	0.0024
160	0.63422	8.46E-04	0.36578	0.00359	0.00185
179	0.73301	7.95E-04	0.3367	0.00327	0.00157
196	0.68474	8.33E-04	0.36526	0.00245	0.0014
239	0.79048	1.00E-03	0.21515	0.00189	0.00119
251	0.57582	7.30E-04	0.42418	0.00142	0.00102
281	0.70548	5.59E-04	0.30452	0.002	9.93E-04
311	0.62874	3.32E-04	0.36226	0.00213	9.88E-04
345	0.641	2.02E-04	0.31102	0.00181	7.29E-04
360	0.73191	4.34E-04	0.31468	8.25E-04	5.52E-04
385	0.82755	3.53E-04	0.29145	8.01E-04	4.70E-04
393	0.71434	1.90E-04	0.27866	0.0013	5.00E-04
426	0.82149	1.27E-04	0.27851	9.39E-04	3.33E-04
440	0.73626	1.06E-04	0.27374	6.69E-04	2.58E-04
485	0.75131	1.18E-04	0.23869	7.27E-04	2.65E-04
508	0.70628	9.89E-05	0.30372	2.03E-04	1.30E-04
535	0.76297	1.04E-04	0.23703	2.63E-04	1.42E-04
550	0.85852	2.28E-05	0.13148	7.60E-04	1.21E-04
575	0.90842	6.91E-05	0.12158	3.43E-04	1.01E-04
590	0.71309	1.16E-05	0.31569	1.65E-04	5.86E-05
613	0.71673	1.16E-05	0.29327	4.75E-05	2.20E-05
635	0.73392	1.07E-05	0.26608	9.95E-05	3.43E-05
676	0.78539	1.23E-05	0.21461	9.40E-05	2.98E-05
699	0.67941	1.25E-05	0.32059	4.40E-05	2.26E-05
729	0.63201	1.09E-05	0.36799	2.20E-05	1.50E-05
754	0.73767	1.03E-05	0.34233	3.36E-05	1.77E-05
786	0.89369	1.10E-05	0.10631	5.89E-05	1.61E-05
815	0.90383	6.18E-06	0.09617	4.97E-05	1.04E-05
830	0.65583	3.65E-06	0.39142	1.72E-05	8.70E-06
864	0.79678	2.74E-06	0.20322	1.88E-05	6.00E-06
873	0.81425	3.71E-06	0.22575	1.19E-05	5.49E-06
906	0.86524	1.30E-06	0.21835	1.41E-05	3.88E-06

Table S2 Parameters of bi-exponential fitting for TPV decay trace (mesoscopic perovskite solar cell).

V_{ph} (mV)	A_1	τ_1 (s)	A_2	τ_1 (s)	τ (s)
26	0.78406	4.00E-04	0.31376	0.00325	0.00121
53	0.83309	8.12E-04	0.2621	0.00515	0.00185
74	0.8366	5.97E-04	0.26023	0.00437	0.00149
101	0.85785	6.80E-04	0.25231	0.0045	0.00155
129	0.85225	6.97E-04	0.25251	0.00458	0.00158
149	0.88754	6.67E-04	0.22749	0.0046	0.00147
171	0.91243	5.67E-04	0.24219	0.00381	0.00125
196	0.7379	4.33E-04	0.37012	0.00308	0.00132
225	0.66937	4.84E-04	0.32685	0.00336	0.00143
251	0.81639	5.14E-04	0.18095	0.00392	0.00113
279	0.68423	2.34E-04	0.32124	0.00164	6.85E-04
294	0.64828	2.32E-04	0.34201	0.00176	7.59E-04
328	0.79212	2.21E-04	0.21824	0.00131	4.55E-04
359	0.75158	1.70E-04	0.26649	0.00111	4.17E-04
380	0.84567	2.30E-04	0.18983	0.00141	4.46E-04
396	0.75345	1.13E-04	0.26291	0.00117	3.85E-04
419	0.84162	1.03E-04	0.2546	0.00103	3.18E-04
439	0.83909	1.29E-04	0.18739	0.00108	3.04E-04
485	0.7606	1.09E-04	0.25146	0.00107	3.46E-04
504	0.7485	1.49E-04	0.28911	9.20E-04	3.63E-04
532	0.8099	9.09E-05	0.22128	9.06E-04	2.66E-04
550	0.69691	1.80E-05	0.37573	1.00E-04	4.67E-05
575	0.82697	9.11E-05	0.21673	7.70E-04	2.32E-04
600	0.65101	8.20E-05	0.39589	3.76E-04	1.93E-04
624	0.73248	5.96E-05	0.25412	1.87E-04	9.24E-05
656	0.70473	2.90E-05	0.2345	5.00E-04	1.47E-04
677	0.78118	2.01E-05	0.23789	3.74E-04	1.03E-04
700	0.82216	2.40E-05	0.23577	3.64E-04	9.98E-05
723	0.80623	3.87E-05	0.22961	1.78E-04	6.95E-05
752	0.80969	3.00E-05	0.18222	1.18E-04	4.62E-05
778	0.71944	2.55E-05	0.22024	1.06E-04	4.44E-05
799	0.7244	1.06E-05	0.26026	1.13E-04	3.78E-05
823	0.73141	8.00E-06	0.29051	7.48E-05	2.70E-05
848	0.68466	1.01E-05	0.32554	3.03E-05	1.66E-05
874	0.88334	1.06E-05	0.1734	2.39E-05	1.28E-05
901	0.79363	9.00E-06	0.2144	2.85E-05	1.32E-05
927	0.74789	4.04E-06	0.25043	1.27E-05	6.21E-06

The trace of TPV is fitted by bi-exponential function is described as: $V(t) = V_{base} + A_1\exp(t/\tau_1) + A_2\exp(t/\tau_2)$, where V_{base} is the baseline, A_1 and A_2 are pre-exponential factors,

and τ_1 and τ_2 are time constants. The charge carried lifetime is calculated as $\tau_n = (A_1\tau_1 + A_2\tau_2)/(A_1 + A_2)$.[1] There is a fast decay phase in the two structures of the devices, which can be attributed to the charge recombination through the perovskite phase. As for the slow recombination process can be caused by the TiO_2 mesoporous for the mesoscopic perovskite solar cell and the trap limited for the planar one.[2,3]

Table S3 Parameters of bi-exponential fitting for TPC decay trace (planar perovskite solar cell).

Light intensity (mw cm^{-2})	A_1	τ_1 (s)	A_2	τ_1 (s)	τ (s)
2.5	0.46978	2.10E-07	0.79069	1.29E-06	8.87E-07
5	0.35242	3.08E-07	0.82161	1.33E-06	1.02E-06
10	0.31732	3.29E-07	0.82985	1.32E-06	1.04E-06
12.5	0.13935	3.34E-07	0.65589	1.34E-06	1.16E-06
15	0.40097	4.53E-07	0.88219	1.38E-06	1.09E-06
20	0.38391	4.27E-07	0.90593	1.36E-06	1.08E-06
22.5	0.37693	4.18E-07	0.91186	1.36E-06	1.08E-06
25	0.34195	3.45E-07	0.82215	1.35E-06	1.05E-06
27.5	0.77993	4.41E-07	0.25595	2.42E-06	9.30E-07
30	0.34346	3.62E-07	0.83702	1.35E-06	1.07E-06
32.5	0.37803	5.37E-07	0.76786	1.39E-06	1.11E-06
35	0.40611	5.03E-07	0.87749	1.37E-06	1.10E-06
37.5	0.43422	2.22E-07	0.81543	1.28E-06	9.09E-07
40	0.26472	3.21E-07	0.94509	1.34E-06	1.11E-06
42.5	0.41829	2.15E-07	0.59983	1.60E-06	1.03E-06
45	0.28619	2.92E-07	0.93123	1.33E-06	1.09E-06
47.5	0.30208	3.44E-07	0.87053	1.31E-06	1.06E-06
50	0.33702	2.52E-07	0.90989	1.28E-06	1.01E-06
52.5	0.33463	3.69E-07	0.84106	1.34E-06	1.06E-06
55	0.40576	4.48E-07	0.88761	1.38E-06	1.09E-06
57.5	0.38344	2.76E-07	0.8776	1.30E-06	9.90E-07
60	0.38067	3.97E-07	0.82724	1.35E-06	1.05E-06
62.5	0.79764	7.62E-07	0.45278	1.79E-06	1.14E-06
70	0.90655	8.29E-07	0.24606	2.35E-06	1.15E-06
72.5	0.7751	1.50E-07	0.29276	3.20E-06	9.85E-07
75	0.62006	2.89E-07	0.3816	2.31E-06	1.06E-06
77.5	0.72243	7.12E-07	0.25472	2.38E-06	1.15E-06
80	0.65242	8.57E-07	0.11673	3.14E-06	1.20E-06
82.5	0.38921	4.75E-07	1.06771	1.78E-06	1.43E-06
85	0.29233	4.38E-06	0.63142	1.26E-06	2.25E-06
87.5	0.37765	2.86E-07	0.65385	3.81E-06	2.52E-06

90	0.30186	5.06E-07	0.69278	3.66E-06	2.70E-06
92.5	0.79001	7.24E-07	0.27271	2.32E-06	1.13E-06
95	0.8057	9.75E-07	0.20479	2.64E-06	1.31E-06
97.5	0.87088	9.69E-07	0.2051	2.72E-06	1.30E-06
100	0.64053	9.98E-07	0.31019	2.17E-06	1.38E-06

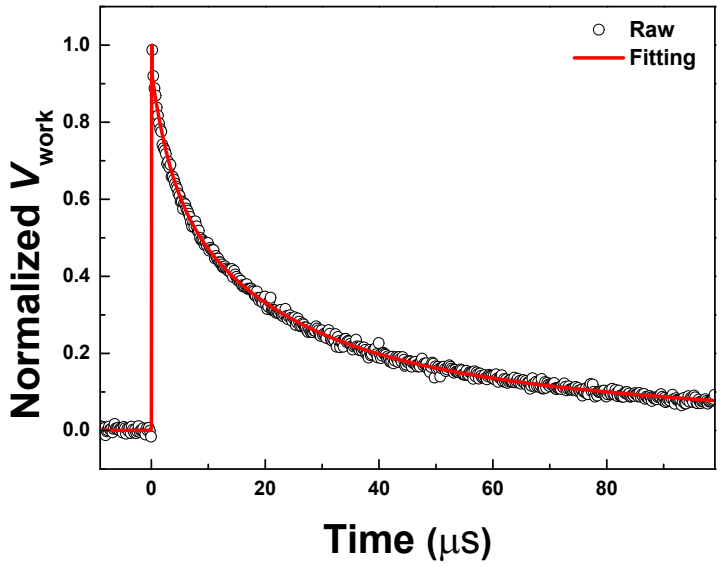
Table S4 Parameters of bi-exponential fitting for TPC decay trace (mesoscopic perovskite solar cell).

Light intensity (mw cm^{-2})	A_1	τ_1 (s)	A_2	τ_1 (s)	τ (s)
2.5	0.46978	2.10E-07	0.79069	1.29E-06	8.87E-07
5	0.35242	3.08E-07	0.82161	1.33E-06	1.02E-06
10	0.31732	3.29E-07	0.82985	1.32E-06	1.04E-06
12.5	0.13935	3.34E-07	0.65589	1.34E-06	1.16E-06
15	0.40097	4.53E-07	0.88219	1.38E-06	1.09E-06
20	0.38391	4.27E-07	0.90593	1.36E-06	1.08E-06
22.5	0.37693	4.18E-07	0.91186	1.36E-06	1.08E-06
25	0.34195	3.45E-07	0.82215	1.35E-06	1.05E-06
27.5	0.77993	4.41E-07	0.25595	2.42E-06	9.30E-07
30	0.34346	3.62E-07	0.83702	1.35E-06	1.07E-06
32.5	0.37803	5.37E-07	0.76786	1.39E-06	1.11E-06
35	0.40611	5.03E-07	0.87749	1.37E-06	1.10E-06
37.5	0.43422	2.22E-07	0.81543	1.28E-06	9.09E-07
40	0.26472	3.21E-07	0.94509	1.34E-06	1.11E-06
42.5	0.41829	2.15E-07	0.59983	1.60E-06	1.03E-06
45	0.28619	2.92E-07	0.93123	1.33E-06	1.09E-06
47.5	0.30208	3.44E-07	0.87053	1.31E-06	1.06E-06
50	0.33702	2.52E-07	0.90989	1.28E-06	1.01E-06
52.5	0.33463	3.69E-07	0.84106	1.34E-06	1.06E-06
55	0.40576	4.48E-07	0.88761	1.38E-06	1.09E-06
57.5	0.38344	2.76E-07	0.8776	1.30E-06	9.90E-07
60	0.38067	3.97E-07	0.82724	1.35E-06	1.05E-06
62.5	0.79764	7.62E-07	0.45278	1.79E-06	1.14E-06
70	0.90655	8.29E-07	0.24606	2.35E-06	1.15E-06
72.5	0.7751	1.50E-07	0.29276	3.20E-06	9.85E-07
75	0.62006	2.89E-07	0.3816	2.31E-06	1.06E-06
77.5	0.72243	7.12E-07	0.25472	2.38E-06	1.15E-06
80	0.65242	8.57E-07	0.11673	3.14E-06	1.20E-06
82.5	0.38921	4.75E-07	1.06771	1.78E-06	1.43E-06
85	0.29233	4.38E-06	0.63142	1.26E-06	2.25E-06
87.5	0.37765	2.86E-07	0.65385	3.81E-06	2.52E-06
90	0.30186	5.06E-07	0.69278	3.66E-06	2.70E-06

92.5	0.79001	7.24E-07	0.27271	2.32E-06	1.13E-06
95	0.8057	9.75E-07	0.20479	2.64E-06	1.31E-06
97.5	0.87088	9.69E-07	0.2051	2.72E-06	1.30E-06
100	0.64053	9.98E-07	0.31019	2.17E-06	1.38E-06

The results of the TPC is also fitted by the by bi-exponential function. The corresponding charge carrier transport nearly exhibits a constant, which can by interpreted by the unique ambipolar transport property of the perovskite.

(a)



(b)

A_1	τ_1 (s)	A_2	τ_1 (s)	τ (s)
0.76929	9.23E-05	0.37427	6.37E-04	2.71E-04

Fig. S4 (a) The representative exponential fitting example of TWVD and (b) the detailed fitting results for the mesoscopic perovskite solar cell.

The trace of TWVD with a bi-exponential function is described as: $V(t) = V_{base} + A_1\exp(t/\tau_1) + A_2\exp(t/\tau_2)$, where V_{base} is the baseline, A_1 and A_2 are pre-exponential factors, and τ_1 and τ_2 are time constants. One can calculate the dynamic time constant as $\tau_n = (A_1\tau_1 + A_2\tau_2)/(A_1 + A_2)$.[1] The mechanism of the charge carrier dynamics process under the working conditions is complex. The charge recombination and transport are competitive and balanced. The competition and balance of carrier output and internal carrier dynamics lead to the bi-exponential decay.

References

1. L. Luo, C. J. Lin, C. S. Hung, C. F. Lo, C. Y. Lin and E. W. Diau, *Phys. Chem. Chem. Phys.*, 2010, **12**, 12973-12977.
2. H. Y. Wang, Y. Wang, M. Yu, J. Han, Z. X. Guo, X. C. Ai, J. P. Zhang and Y. Qin, *Phys. Chem. Chem. Phys.*, 2016, **18**, 12128-12134.
3. M. Yu, Y. Wang, H.-Y. Wang, J. Han, Y. Qin, J.-P. Zhang and X.-C. Ai, *Chem. Phys. Lett.*, 2016, **662**, 257-262.