

## Enhanced photovoltaic performance with co-sensitization of porphyrin and an organic dye in dye-sensitized solar cells

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We designed a stepwise approach for co-sensitization of a zinc porphyrin sensitizer (LD12) with a spirally configured organic dye (CD5) for dye-sensitized solar cells. The co-sensitized LD12 + CD5 device showed significantly enhanced  $V_{OC}$  and  $J_{SC}$  relative to its individual single-dye sensitized devices. Upon optimization, the device made of the LD12 + CD5 system yielded  $J_{SC}/\text{mA cm}^{-2} = 16.7$ ,  $V_{OC}/V = 0.74$ ,  $FF = 0.73$  and  $\eta = 9.0\%$ ; this performance is superior to that of either individual device made from LD12 ( $\eta = 7.5\%$ ) and CD5 ( $\eta = 5.7\%$ ) under the same conditions of fabrication. To understand the effects of the potential shift and charge recombination on the cell performance, we measured charge-extraction (CE) and intensity-modulated photovoltage spectra (IMVS). Upon sensitization with each dye, the  $\text{TiO}_2$  potentials are similar, but co-sensitization causes the potential to shift down (cathodic shift). Charge recombination was significantly retarded for the co-sensitized system relative to each individual dye-sensitized

system, to account for the enhanced  $V_{OC}$  for the former relative to the latter. A test of stability indicates a systematic trend between the LD12 + CD5 and LD12 devices; the performance of the co-sensitized device degraded only  $\sim 15\%$  and remained stable during the period of 500–1000 h near 295 K.

Dye-sensitized solar cells (DSSC) attract much attention because of their great advantages—light weight, low cost and easy processing, with colorful and transparent features as next-generation photovoltaic devices.<sup>1</sup> Photosensitizers such as ruthenium complexes,<sup>2</sup> zinc porphyrin<sup>3</sup> and a metal-free organic dye<sup>4</sup> have been developed to serve as efficient light harvesters for DSSC. The devices made of ruthenium complexes<sup>5</sup> and a porphyrin sensitizer<sup>6</sup> have attained remarkable efficiencies,  $\eta = 11.0\text{--}11.5\%$ , of power conversion under one-sun illumination. For comparison, with a cobalt-based redox electrolyte, the efficiency of the device made from a push-pull zinc porphyrin (YD2-*o*-C8) attained 11.9%,<sup>7</sup> whereas a system co-sensitized with an organic dye (Y123) boosted the cell performance to  $\eta = 12.3\%$ ,<sup>7</sup> which is a new milestone in this research field, stimulating investigation of the development of key materials to promote the device performance.

Co-sensitization is an effective approach to enhance the device performance through a combination of two or more dyes sensitized on semiconductor films together, extending the light-harvesting ability so as to increase the photocurrents of the devices. For example, the co-sensitization of two organic dyes (JK2 and SQ1) with

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### Broader context

Co-sensitization of two or more dyes with complementary absorption spectra on  $\text{TiO}_2$  film is a well-known strategy to further enhance the light-harvesting ability of dye-sensitized solar cells (DSSC). There are two ways to make a co-sensitization: the cocktail approach makes the co-sensitization in a mixed dye solution with certain molar ratios of the two dyes, whereas the stepwise approach accomplishes adsorption of the two different dyes in a consecutive manner. Here we followed a stepwise approach to make the co-sensitization of porphyrin with an organic dye for which the co-sensitized device exhibited enhancements of photovoltaic performance not only in  $J_{SC}$  but also in  $V_{OC}$ . We found that co-sensitization stabilizes the potential of  $\text{TiO}_2$  but it also effectively retards the charge recombination to lead to the enhanced  $V_{OC}$ , which is unprecedented for the porphyrin + organic dye co-sensitization system. Porphyrins are known to suffer from dye aggregation due to their planar structural nature. In the present study we have shown that co-sensitization of a zinc porphyrin with a well-designed organic dye does help in changing the aggregation morphology of the porphyrin adsorbed on  $\text{TiO}_2$  film to further improve its device performance.

complementary spectral responses showed an enhanced photovoltaic performance relative to the devices fabricated with the individual dyes;<sup>8</sup> phthalocyanine dye (TT1) co-sensitized with various organic dyes (JK2 or D2) exhibited an enhanced device performance through the improved light-harvesting efficiency of the cell;<sup>9</sup> co-sensitization of TiO<sub>2</sub> films with a black dye and organic dyes (D131 or Y1) resulted in a significantly enhanced photocurrent such that the device performance attained  $\eta = 11.0\text{--}11.4\%$ .<sup>10</sup> For porphyrins, a device based on co-sensitization of a TiO<sub>2</sub> film (thickness 2.4  $\mu\text{m}$ ) with YD2 and an organic dye (D205) showed a short-circuit current density ( $J_{\text{SC}}$ ) increase by 20%,<sup>6</sup> but for the champion system (YD2-*o*-C8 with Y123) the enhancement in  $J_{\text{SC}}$  was limited (17.3 vs. 17.7  $\text{mA cm}^{-2}$ ) because the gap between the Soret and the Q bands in the IPCE spectrum for the porphyrin-alone device was small.<sup>7</sup> For most co-sensitization systems above,<sup>6-9</sup> the values of the open-circuit voltage ( $V_{\text{OC}}$ ) are between those of the separate individual single-dye sensitized devices, which limits the enhancement of the overall device performance.

Here we report a promising DSSC system based on a zinc porphyrin bearing two *ortho*-substituted long alkoxy chains (LD12)<sup>11</sup> co-adsorbed with a spirally configured donor-acceptor organic dye (CD5).<sup>12</sup> The syntheses and characterizations of these novel photosensitizers are published elsewhere;<sup>11,12</sup> the corresponding molecular structures appear in Chart 1. Both  $J_{\text{SC}}$  and  $V_{\text{OC}}$  of the co-sensitized devices were significantly enhanced relative to their corresponding single-dye sensitized devices, improving the overall performance for the LD12 + CD5 device by 20% and 58% with respect to LD12 and CD5 single-dye devices. To understand how the  $V_{\text{OC}}$  enhancement arose, we measured charge-extraction (CE)<sup>13</sup> and intensity-modulated photovoltage spectra (IMVS).<sup>14</sup>

Fig. 1a and b show the absorption spectra of LD12 and CD5 in THF solutions and on TiO<sub>2</sub> films, respectively. For LD12, the Soret band of the thin-film spectrum was significantly broadened relative to that in solution; the maximum shifted from 442 nm to 447 nm, a spectral feature similar to that reported for a push-pull porphyrin (LD16).<sup>15</sup> Upon co-sensitization with CD5 on TiO<sub>2</sub> film, the maximum of the Soret band of LD12 shifted back to 443 nm. This observation indicates that aggregations of both H- (parallel orientation) and J-type (tilted orientation) occur for LD12 adsorbed on TiO<sub>2</sub>, but co-sensitization with CD5 adjusts the arrangement of the porphyrin molecules toward a more nearly parallel configuration on the surface of TiO<sub>2</sub>. The absorption spectrum of CD5 complements that of LD12 for the co-sensitized film showing the panchromatic feature to render an optimal light-harvesting effect in the region of 350–650 nm.

The co-sensitization of LD12 with CD5 on a TiO<sub>2</sub> film<sup>11</sup> of thickness  $\sim 20 \mu\text{m}$  was achieved *via* a stepwise approach: the TiO<sub>2</sub> electrode was immersed in the LD12 solution for 3 h and then

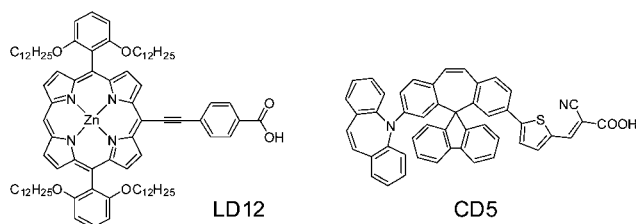


Chart 1 Molecular structures of LD12 and CD5.

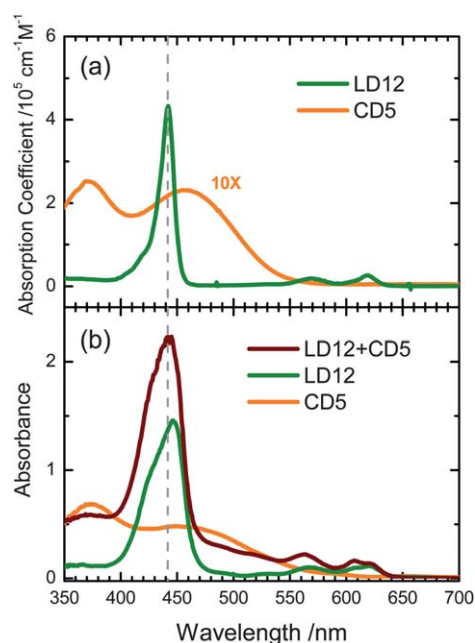


Fig. 1 Absorption spectra of (a) LD12 and CD5 in THF and (b) LD12, CD5 and LD12 + CD5 sensitized on TiO<sub>2</sub> films (thickness 2  $\mu\text{m}$ ). The absorption coefficients of CD5 in (a) are magnified 10 times; the dashed gray line indicates the peak absorption ( $\lambda = 442 \text{ nm}$ ) of the Soret band of LD12 in solution.

immersed in the CD5 solution for 2 h. Afterwards, the LD12 + CD5 co-sensitized film was assembled into a DSSC device of sandwich type with a Pt-coated counter electrode and filled with an appropriate

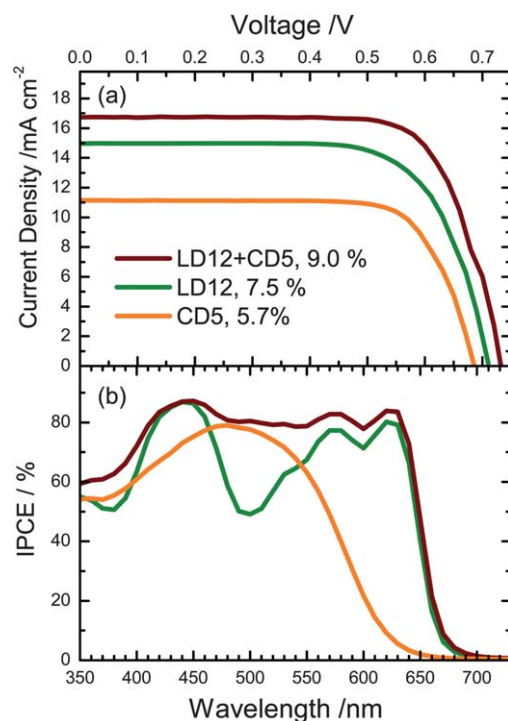


Fig. 2 Optimized photovoltaic properties: (a) current-voltage characteristics and (b) the corresponding IPCE action spectra of devices made of LD12, CD5, and LD12 + CD5 with the same fabricated TiO<sub>2</sub> films (17 + 5  $\mu\text{m}$ ) under one-sun AM-1.5G irradiation.

electrolyte. Fig. 2a and b show the current–voltage characteristics and the corresponding IPCE action spectra, respectively, for a comparison of the photovoltaic performance of the LD12 + CD5 co-sensitized device with that of either individual dye-sensitized device; the corresponding photovoltaic parameters are summarized in Table 1. The results clearly show that, upon co-sensitization, the performance of the LD12 + CD5 device improved to yield  $J_{SC}/\text{mA cm}^{-2} = 16.7$ ,  $V_{OC}/V = 0.74$ ,  $FF = 0.73$  and  $\eta = 9.0\%$ ; the latter is significantly greater than  $\eta = 7.5\%$  for LD12 and  $\eta = 5.7\%$  for CD5 in the separate devices under the same conditions of fabrication.

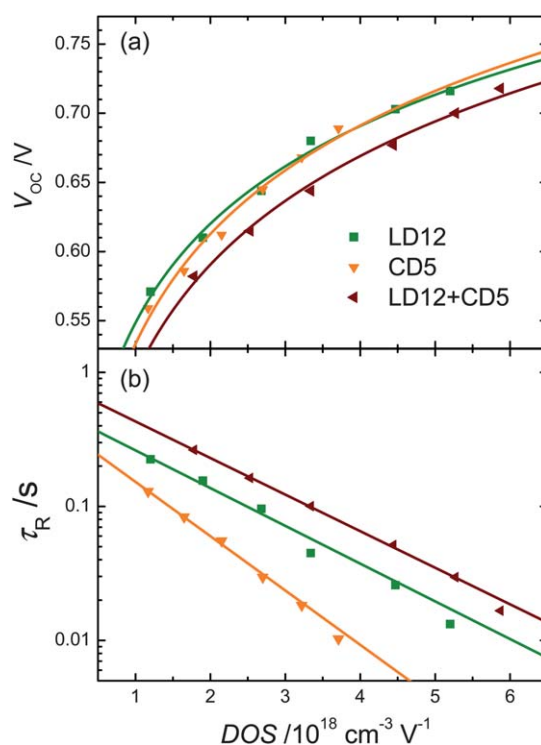
For the co-sensitized system, the enhancement of  $J_{SC}$  is understandable from the IPCE spectra shown in Fig. 2b; the gap of the photoresponse of about 500 nm for the LD12 device was filled in the action spectrum of the LD12 + CD5 device by the contribution of CD5 that shows its maximum photoresponse in that spectral region. As a result,  $J_{SC}$  of the co-sensitized device increased from  $14.97 \text{ mA cm}^{-2}$  to  $16.74 \text{ mA cm}^{-2}$  to contribute  $\sim 12\%$  enhancement of the overall performance.  $V_{OC}$  of the co-sensitized device increased from 0.711 V (LD12) and 0.689 V (CD5) to 0.736 V, which is unprecedented for reported co-sensitized porphyrin and organic-dye systems.<sup>6–9</sup>

To account for the enhanced  $V_{OC}$  upon co-sensitization, we derived the shift of the conduction band of  $\text{TiO}_2$  by measuring the charge densities ( $N_c$ ) for the three devices at each  $V_{OC}$  with the CE method, and converted the  $N_c$  values into the density of states (DOS) via  $\text{DOS} = N_c/V_{OC}$ .<sup>16</sup> Fig. 3a displays plots of  $V_{OC}$  vs. DOS for the three systems at six intensities of white light from a LED. The CE results indicate that the  $\text{TiO}_2$  potentials of the LD12 and CD5 devices are similar to each other, but that of the LD12 + CD5 device exhibits a potential shift down (cathodic shift)  $\sim 25 \text{ mV}$  with respect to the individual dye-sensitized devices. Co-sensitization of LD12 with CD5 on a  $\text{TiO}_2$  film has thus the effect to stabilize the  $\text{TiO}_2$  potential, which we explain as follows. As shown in Fig. 1 the spectral broadening feature indicates that LD12 molecules aggregate in two geometries on the surface of  $\text{TiO}_2$ ; the blue spectral shift corresponds to the parallel (H-type) and the red shift to the tilted (J-type) orientations. Co-sensitization of LD12 with CD5 on  $\text{TiO}_2$  would produce a blue shift of the Soret band, indicating that the LD12 molecules adjust to a more nearly parallel conformation so as to leave space for the CD5 co-sensitizer. Such a structural modification would allow an additive (e.g.,  $\text{Li}^+$ ) to reach a new equilibrium state on the surface of  $\text{TiO}_2$  such that a lower potential is observed. The stabilization of the co-sensitized system in this case cannot account for the observed  $V_{OC}$  enhancement for the LD12 + CD5 system, for which we performed IMVS measurements to obtain kinetic information about the charge recombination of the system.

We measured IMVS with a AC perturbation (modulation 10%) superimposed on the six CW bias light intensities, the same as in the

**Table 1** Optimized photovoltaic parameters of DSSC fabricated with LD12, CD5, or LD12 + CD5 adsorbed on the  $\text{TiO}_2$  films of thickness  $(15 + 5) \mu\text{m}$  under simulated AM-1.5G illumination (power  $100 \text{ mW cm}^{-2}$ ) and active area  $0.16 \text{ cm}^2$

Dye	$J_{SC}/\text{mA cm}^{-2}$	$V_{OC}/V$	FF	$\eta$ (%)
LD12	14.97	0.711	0.705	7.5
CD5	11.12	0.689	0.744	5.7
LD12 + CD5	16.74	0.736	0.731	9.0



**Fig. 3** (a) Open-circuit voltage ( $V_{OC}$ ) and (b) electron lifetimes ( $\tau_R$ ) as a function of density of states (DOS) for the devices made of LD12 alone, CD5 alone and their co-sensitized combination.

CE experiments, in the frequency range of 0.1–1000 Hz; the frequency of the minimum IMVS response corresponds to the inverse of the electron lifetime ( $\tau_R$ ) of the device at the open-circuit condition. Fig. 3b shows plots of  $\tau_R$  vs. DOS for the three systems at the six light intensities. The results indicate a systematic trend with the electron lifetimes (corresponding to the degree of charge recombination) showing the order LD12 + CD5 > LD12 > CD5, which is consistent with the variation of  $V_{OC}$  showing the same order. Our results are consistent with those of the black dye + Y1 co-sensitized system showing an increase of  $\sim 20 \text{ mV}$  in  $V_{OC}$ , which is also explicable according to the electron lifetimes increased upon co-sensitization.<sup>10b</sup> For the TT1 + D2 co-sensitized system, these observed lifetimes in the co-sensitized device are between those of the D2 and the TT1 devices, correlating well with the trend of  $V_{OC}$ .<sup>9b</sup> Based on the cobalt redox electrolyte, the decreased  $V_{OC}$  of the YD2-*o*-C8 + Y123 device relative to that of the device containing only the YD2-*o*-C8 dye is also explicable by the smaller electron lifetimes for the former than for the latter.<sup>7</sup> In our case, we observed that  $V_{OC}$  became enhanced upon co-sensitization of LD12 with CD5; this result is due to the effect of a retarded charge recombination even though the potential of  $\text{TiO}_2$  shifted slightly down. We regard such a retardation as due to an effective combination between zinc porphyrin with long alkoxy chains and the organic dye with bulky spiral *cis*-stilbene/fluorene hybrids, such that they formed a compact layer on the surface of  $\text{TiO}_2$  to impede the approach of triiodide anions in the electrolyte to the  $\text{TiO}_2$  surface.

We tested the stability (for a period of 1000 h) near 295 K for the three devices—co-sensitized LD12 + CD5, LD12 alone, and CD5 alone. Fig. 4a–d show the temporal variations of  $J_{SC}$ ,  $V_{OC}$ , FF and  $\eta$  for the three systems. The results indicate that the LD12 + CD5

device attained the best performance ( $\eta \approx 9\%$ ) during the period of 40–140 h; the efficiency then decreased to 8.1% at 300 h and further to 7.7% at 500 h. After 500 h, the performance of the co-sensitized device remained stable until the end of the test (1000 h). The degraded efficiency of the LD12 + CD5 device reflects mainly the decreased  $J_{SC}$ , from 16.7  $\text{mA cm}^{-2}$  at 40 h to 14.7  $\text{mA cm}^{-2}$  at 500 h, whereas the  $V_{OC}$  and the FF values remained approximately constant during the entire period. The degraded performance of the LD12 device is also due to the decreased  $J_{SC}$ , but that of the CD5 device is mainly due to the decreased  $V_{OC}$ . A decrease of  $J_{SC}$  implies a possible desorption of the dye molecules from the  $\text{TiO}_2$  surface for decreased light harvesting, whereas the decreased  $V_{OC}$  might be due to an altered ionic equilibrium on the  $\text{TiO}_2$  surface for a shift down of the potential or for an increased recombination of charge. As the trend of performance degradation of the co-sensitized device is similar to that of the LD12 device, we conclude that the degradation of  $\sim 15\%$  of the cell performance in the initial 500 h results from desorption of some porphyrin molecules weakly bound to the  $\text{TiO}_2$  surface.

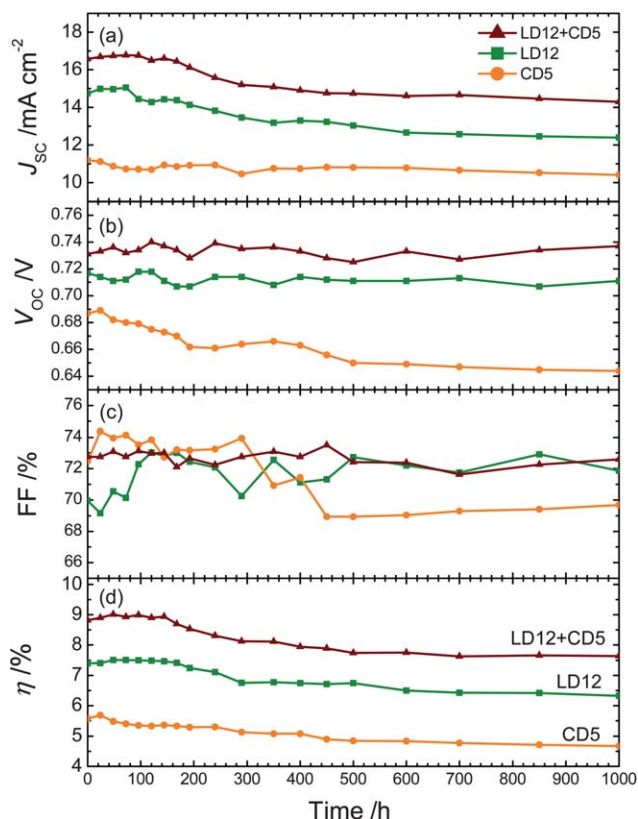
In conclusion, we have designed a co-sensitized system with a zinc porphyrin enveloped with long alkoxy chains (LD12) and a spirally structured push-pull organic dye (CD5); the co-sensitized device exhibits significant improvement not only of  $J_{SC}$  but also of  $V_{OC}$ , yielding an overall efficiency of 9.0% greater than that of a device containing only the porphyrin (7.5%) or the organic dye (5.7%).  $J_{SC}$  is enhanced because of the combined light-harvesting effect of the two

dyes that have complementary absorption spectra, and  $V_{OC}$  is enhanced because the retarded charge recombination overwhelmed the shift down of the  $\text{TiO}_2$  potential. In the test of stability, the performance of the co-sensitized device remained stable after 500 h with prior degradation by only  $\sim 15\%$ . The present work can thus provide guidance, with appropriate molecular design, to seek more promising co-sensitized systems with the ability to harvest an increased portion of the solar spectrum and to enhance the photovoltage. Work is in progress in this direction.

## Experimental

The LD12, CD5 and LD12 + CD5 co-sensitized devices were fabricated with a working electrode based on  $\text{TiO}_2$  nanoparticles (NP) and a Pt-coated counter electrode reported elsewhere.<sup>11,12</sup> For the working electrode, a paste composed of  $\text{TiO}_2$  NP (particle size  $\approx 25$  nm) prepared with a sol-gel method for the transparent nanocrystalline layer was coated on a  $\text{TiCl}_4$ -treated FTO glass substrate (TEC 7, Hartford, USA) to obtain the required thickness of the film with repetitive screen printing. To improve the performance of the device, we screen-printed an additional scattering layer (particle size  $\approx 300$  nm) on the transparent active layer. The  $\text{TiO}_2$  electrode was immersed in a solution containing LD12 (0.15 mM) and CDCA (10 mM) in ethanol/toluene (volume ratio 4 : 1) at 25 °C for 3 h. Afterwards, this LD12-sensitized film was washed in absolute ethanol, dried in air, and immersed in a solution containing CD5 (0.15 mM) and CDCA (0.3 mM) in ethanol and kept at 25 °C for 2 h. The co-sensitized working electrode was assembled with the counter electrode into a cell of sandwich type and sealed with a hot-melt film (SX1170, thickness 60  $\mu\text{m}$ ) at 90 °C. The electrolyte solution containing LiI (0.1 M),  $\text{I}_2$  (0.05 M), PMII (1.0 M), and 4-*tert*-butylpyridine (0.5 M) in a mixture of acetonitrile and valeronitrile (volume ratio 85 : 15) was introduced into the space between the two electrodes, so completing the fabrication of these DSSC devices. The photovoltaic performance of the device was assessed through measurement of an  $I$ - $V$  curve with a solar simulator (AM-1.5G, XES-502S, SAN-EI) calibrated with a standard silicon reference cell (Oriel PN 91150V, VLSI standards). The incident monochromatic efficiencies for conversion from photons to current (IPCE) spectra of the corresponding devices were measured with a system comprising a Xe lamp (PTi A-1010, 150 W), a monochromator (PTi, 1200  $\text{g mm}^{-1}$  blazed at 500 nm), and a source meter (Keithley 2400, computer-controlled). A standard Si photodiode (Hamamatsu S1337-1012BQ) served as a reference to calibrate the power density of the lamp at each wavelength.

The intensity-modulated photovoltage spectra (IMVS) were measured with the CIMPS equipment (Zahner) at an open-circuit condition based on a CW while light at six intensities (0.03–1.1  $\text{W cm}^{-2}$ ) controlled with a slave system (XPOT, Zahner) to obtain the photovoltaic response induced by the modulated light. The modulated light was driven with a 10% AC perturbation current superimposed on a DC current in a frequency range from 0.1 to 1000 Hz. The measurements of charge extraction (CE) were performed with the same CIMPS system under the same bias light irradiations. For that experiment, the system was initially set to an open-circuit condition for 10 s for the photovoltage of the device to attain a steady state; the white light from the LED was then terminated while the device simultaneously switched to a short-circuit condition to extract the charges generated at that bias light intensity.



**Fig. 4** A test of stability of devices over 1000 h showing the degradation of the photovoltaic performance for (a) short-circuit current density ( $J_{SC}$ ), (b) open-circuit voltage ( $V_{OC}$ ), (c) fill factor (FF) and (d) efficiency ( $\eta$ ) of power conversion for the devices made of LD12 alone, CD5 alone and their co-sensitized combination.

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