

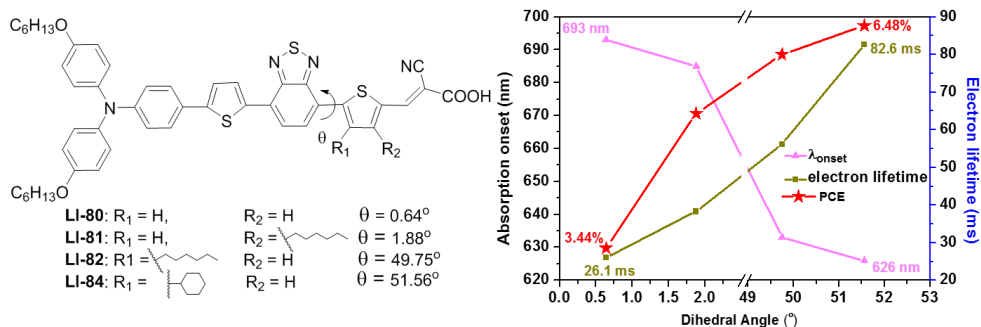
# Significantly Improved Performance of Dye-Sensitized Solar Cell by Optimizing Organic Dyes with Pyrrole as the Isolation Spacer and Utilizing Alkyl Chain Engineering

Jinfeng Wang,<sup>a</sup> Siwei Liu,<sup>a</sup> Zhaofei Chai,<sup>a</sup> Kai Chang,<sup>a</sup> Manman Fang,<sup>a</sup> Mengmeng Han,<sup>a</sup> Yiyi Wang,<sup>a</sup> Sheng Li,<sup>b</sup> Hongwei Han,<sup>b</sup> Qianqian Li,<sup>\*a</sup> Zhen Li<sup>a</sup>

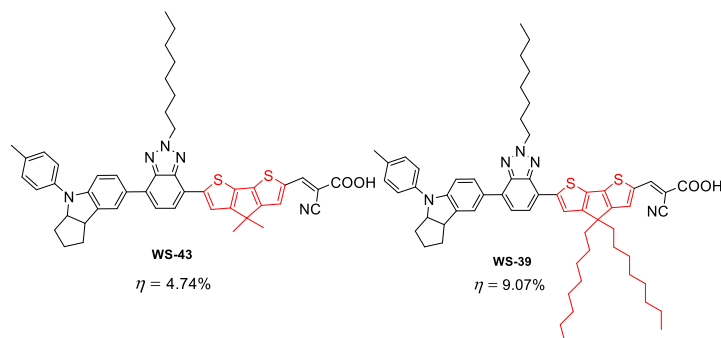
## Content

<b>Additional graphs</b> .....	2
Chart S1 The relationship of absorption onset, electron lifetime and conversion efficiency of the corresponding DSCs based on LI-80-LI-82 and LI-84.....	2
Chart S2. The chemical structures of WS-43 and WS-39.....	2
Figure S1. Absorption spectra of dyes on TiO <sub>2</sub> films with thickness 9 μm. ....	3
Figure S2 Cyclic voltammograms of dyes in CH <sub>2</sub> Cl <sub>2</sub> solution .....	3
Table S1. Optical and Electrochemical Properties of dyes .....	3
Table S2. Frontier orbitals and optimized structures of sensitizers .....	3
Figure S3. The changes of NBO charge from ground state to excited state in dye LI-80 and LI-121.....	4
Table S3. Photovoltaic performance of DSCs based on sensitizers.....	4
Figure S4. EIS spectra of DSCs tested in the dark: Nyquist plots (A) and Bode phase (B).....	5
Figure S5. <i>J-V</i> characteristic curves (A) and IPCEs (B) for DSCs based on LI-124 with the addition of CDCA .....	5
Figure S6. Charge density (A) and electron lifetime (B) at open circuit as a function of V <sub>oc</sub> for DSCs based on LI-124/CDCA-sensitized solar cells. ....	5
Figure S7. EIS spectra of DSCs tested at 0.69V forward bias in the dark: Nyquist plots (A) and Bode phase (B) .....	5
Table S4. Photovoltaic performance of DSCs based on LI-124/CDCA .....	5
Figure S8. Simulated adsorption models for sensitizers LI-121, LI-124 and LI-124/CDCA.....	6
Figure S9. The storage stability of DSCs based on LI-121(left) and LI-122(right).....	6
Figure S10. The storage stability of DSCs based on LI-123 (left) and LI-125 (right).....	6
Figure S11. The absorption spectra of LI-124 on TiO <sub>2</sub> film after full sun-light irradiation.....	7
Figure S12. The absorption spectra of LI-121-123 and LI-125 on TiO <sub>2</sub> film after full sun-light irradiation .....	7
Figure S13. The picture of dyes on TiO <sub>2</sub> films before and after full sun-light irradiation.....	8
Figure S14. TGA curves of LI-121-LI-125.....	8

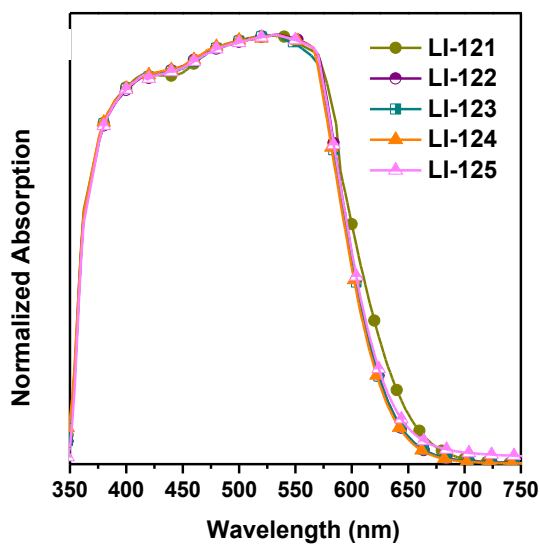
## Additional graphs



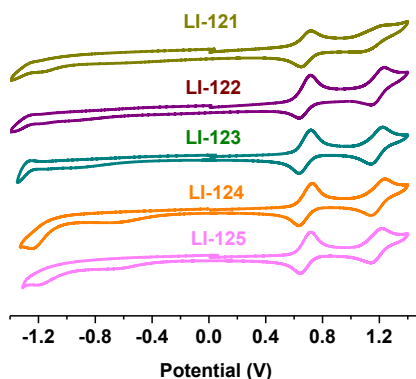
**Chart S1** The relationship of absorption onset, electron lifetime and conversion efficiency of the corresponding DSCs based on LI-80-LI-82 and LI-84



**Chart S2.** The chemical structures of WS-43 and WS-39



**Figure S1.** Absorption spectra of dyes on TiO<sub>2</sub> films (9 μm)



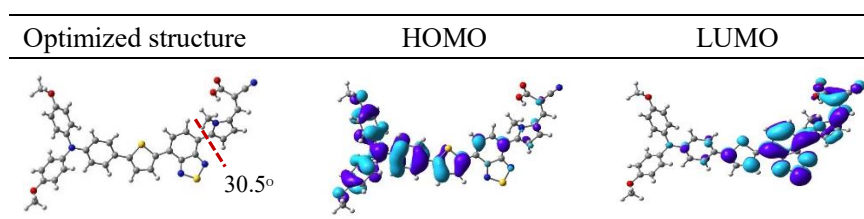
**Figure S2** Cyclic voltammograms of dyes in CH<sub>2</sub>Cl<sub>2</sub> solution

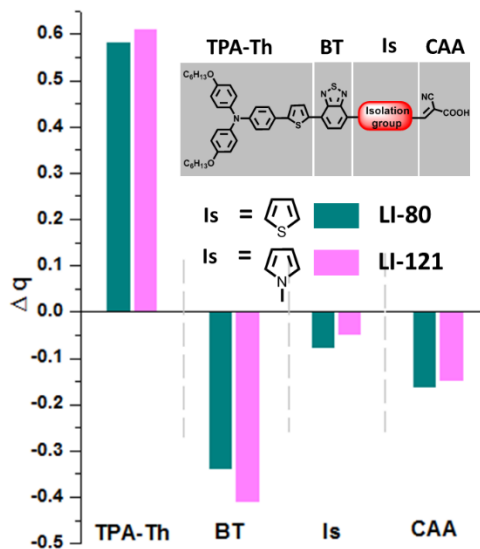
**Table S1.** Optical and Electrochemical Properties of dyes

dye	$\lambda_{\text{abs}}^a$ [nm]	$E_{0-0}^b$ [V]	$E_{\text{ox}}^c$ [V]	$E_{\text{ox}}^{*d}$ [V]
<b>LI-121</b>	379, 516	1.97	0.79	-1.18
<b>LI-122</b>	382, 516	2.00	0.80	-1.20
<b>LI-123</b>	382, 517	1.99	0.80	-1.19
<b>LI-124</b>	382, 517	1.99	0.81	-1.19
<b>LI-125</b>	381, 517	2.00	0.80	-1.20

<sup>a</sup>Absorption spectra of dyes measured in CH<sub>2</sub>Cl<sub>2</sub> (30 μM). <sup>b</sup>The bandgap  $E_{0-0}$  was derived from the observed optical edge. <sup>c</sup> $E_{\text{ox}}$  were measured in CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M TBAPF<sub>6</sub> as electrolyte. The oxidation potential ( $E_{\text{ox}}$ ) referenced to calibrated Ag/AgCl was converted to the NHE reference scale:  $E_{\text{ox}} = E_{\text{ox}}^{\text{on}} + 0.2$ , <sup>d</sup> $E_{\text{ox}}^*$  was calculated from  $E_{\text{ox}} - E_{0-0}/e$ .

**Table S2.** Frontier orbitals and optimized structures of sensitizers (The alkyl chains were simplified with methyl moiety)



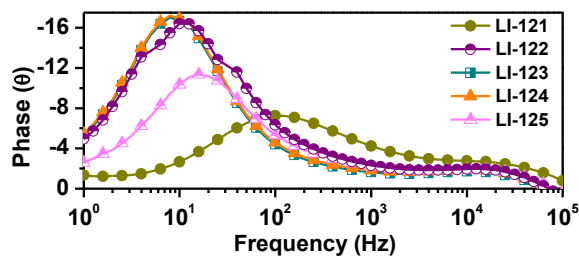
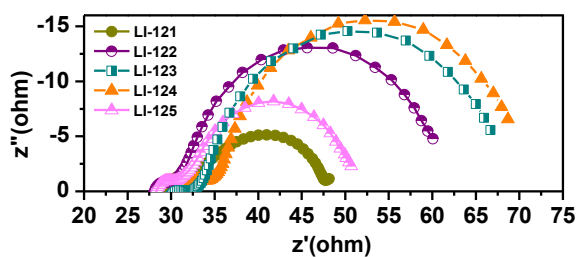


**Figure S3.** The changes of NBO charge from ground state to excited state in dye **LI-80** and **LI-121**

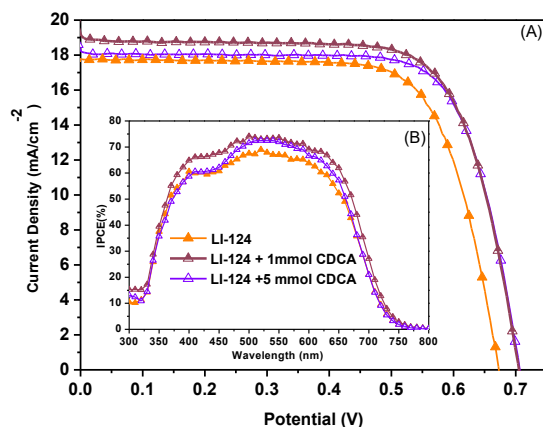
**Table S3.** Photovoltaic performance of DSCs based on sensitizers

Dye	$J_{sc}$ [mA cm <sup>-2</sup> ]	$V_{oc}$ [mV]	$FF$	$\eta$ [%]	DLA
<b>LI-121</b>	9.83±0.21	598±5	0.73±0.01	4.27±0.21	3.29
<b>LI-122</b>	15.22±0.54	661±4	0.69±0.01	6.94±0.21	2.97
<b>LI-123</b>	17.63±0.18	673±3	0.72±0.01	8.54±0.13	2.87
<b>LI-124</b>	17.78±0.25	674±4	0.73±0.01	8.75±0.11	2.80
<b>LI-125</b>	16.30±0.60	618±3	0.72±0.01	7.25±0.18	2.41
<b>N719</b>	16.76±0.21	683±3	0.72±0.01	8.26±0.21	----

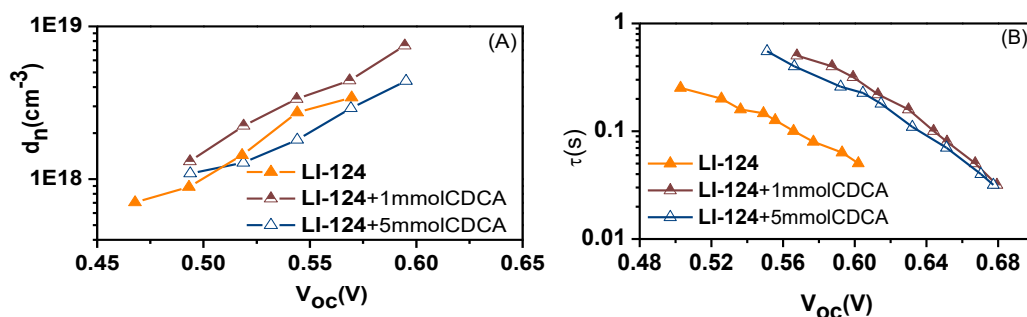
DLA refer to dye-loading amount [ $10^{-8}$ mol cm<sup>-2</sup>μm<sup>-1</sup>]



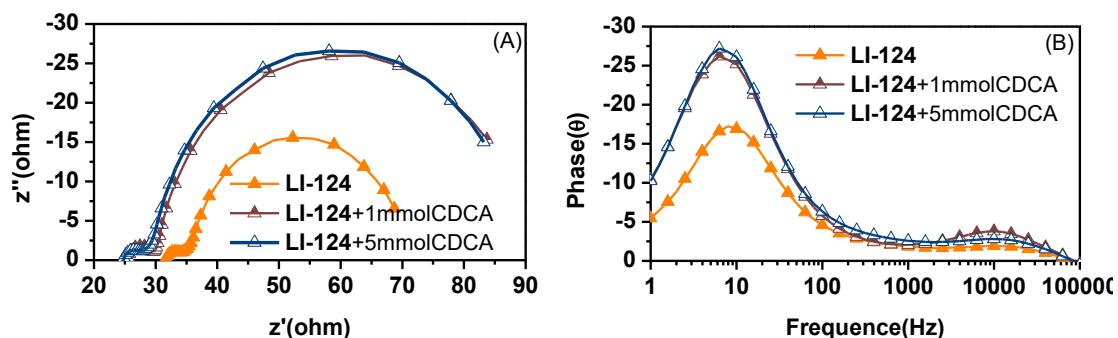
**Figure S4.** EIS spectra of DSCs tested in the dark: Nyquist plots (A) and Bode phase (B)



**Figure S5.**  $J$ - $V$  characteristic curves (A) and IPCEs (B) for DSCs based on **LI-124** with the addition of CDCA



**Figure S6.** Charge density (A) and electron lifetime (B) at open circuit as a function of  $V_{oc}$  for DSCs based on **LI-124/CDCA**-sensitized solar cells.



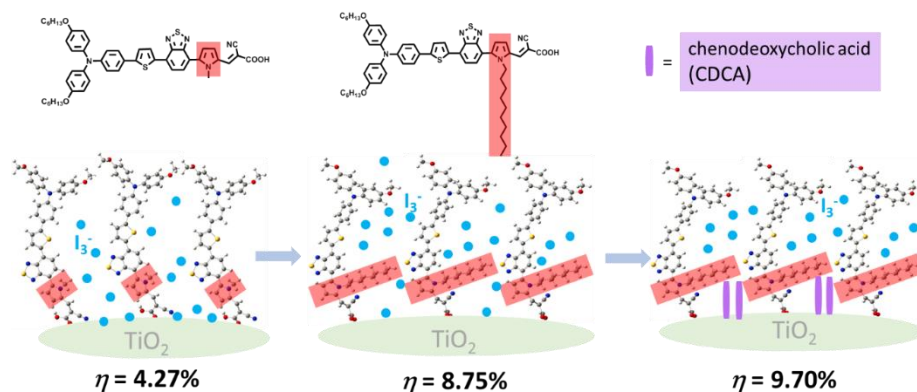
**Figure S7.** EIS spectra of DSCs tested at 0.69V forward bias in the dark: Nyquist plots (A) and Bode phase (B)

**Table S4.** Photovoltaic performance of DSCs based on **LI-124/CDCA**

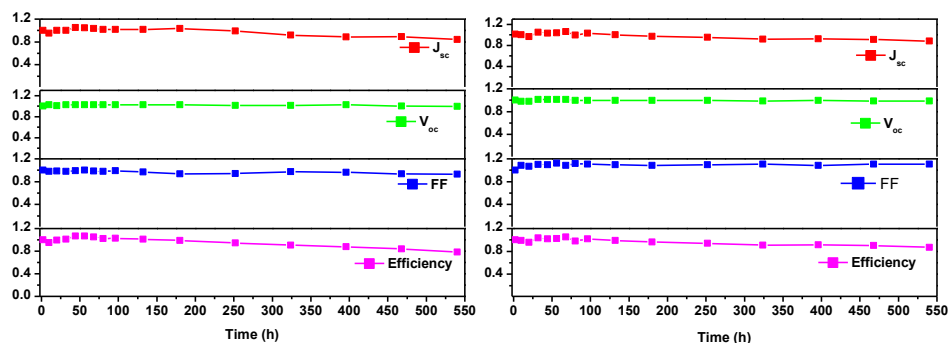
Dye	CDCA	$J_{sc}$ [mA cm <sup>-2</sup> ]	$V_{oc}$ [mV]	$FF$	$\eta$ [%]	DLA
-----	------	---------------------------------	---------------	------	------------	-----

	0	17.78±0.25	674±4	0.73±0.01	8.75±0.11	2.80
<b>LI-124</b>	1	18.96±0.50	710±5	0.70±0.01	9.70±0.27	2.47
	5	18.08±0.23	710±4	0.73±0.01	9.37±0.11	1.99

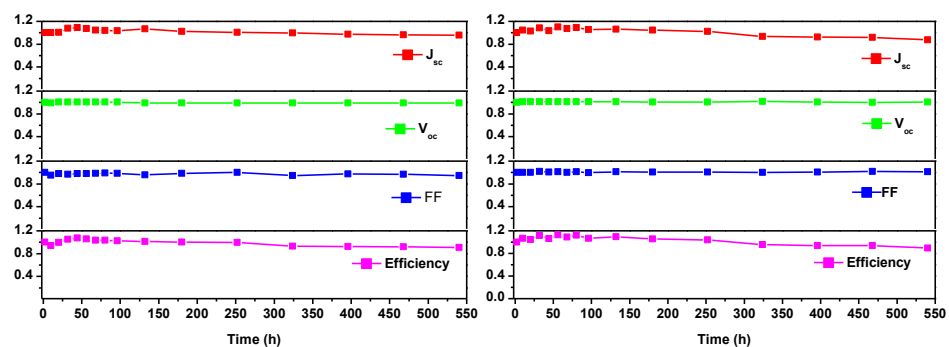
DLA is the abbreviation of dye-loading amount [ $10^{-8}\text{mol cm}^{-2}\mu\text{m}^{-1}$ ]



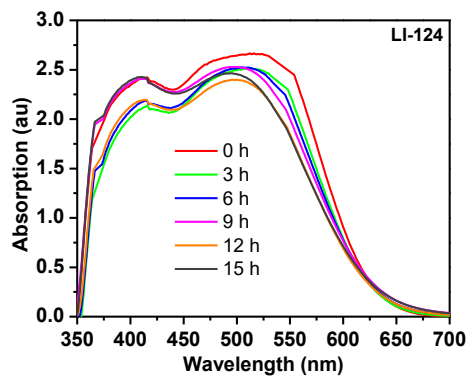
**Figure S8.** Simulated adsorption models for sensitizers **LI-121**, **LI-124** and **LI-124/CDCA**



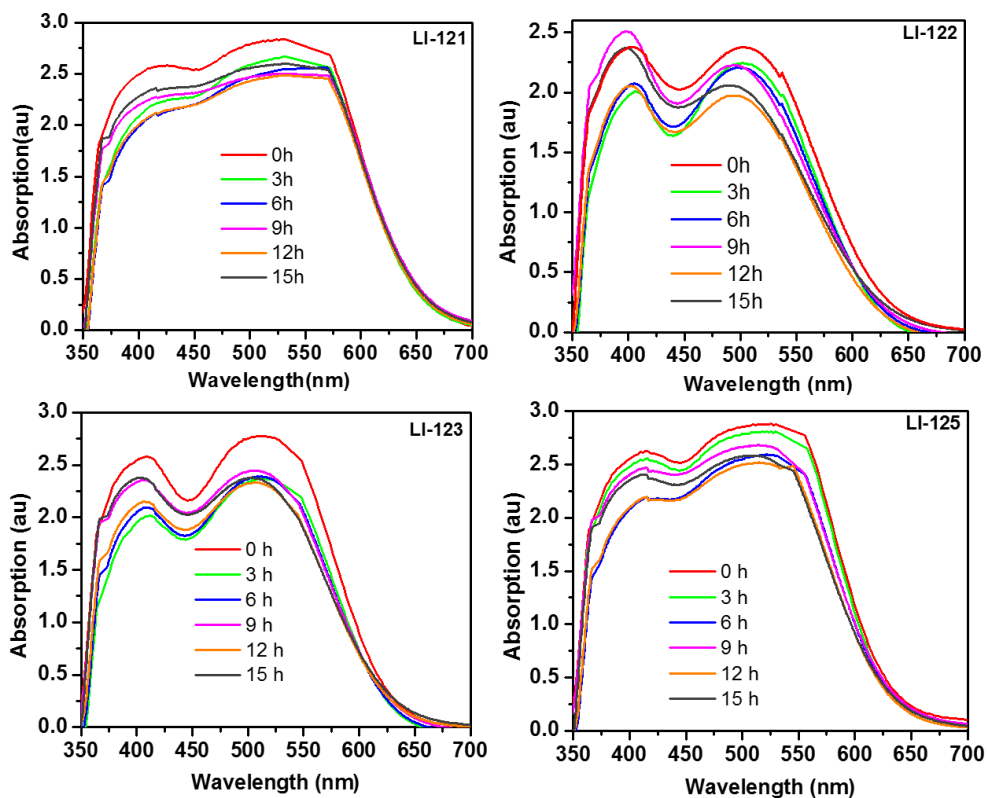
**Figure S9.** The storage stability of DSCs based on **LI-121**(left) and **LI-122**(right)



**Figure S10.** The storage stability of DSCs based on **LI-123** (left) and **LI-125** (right)

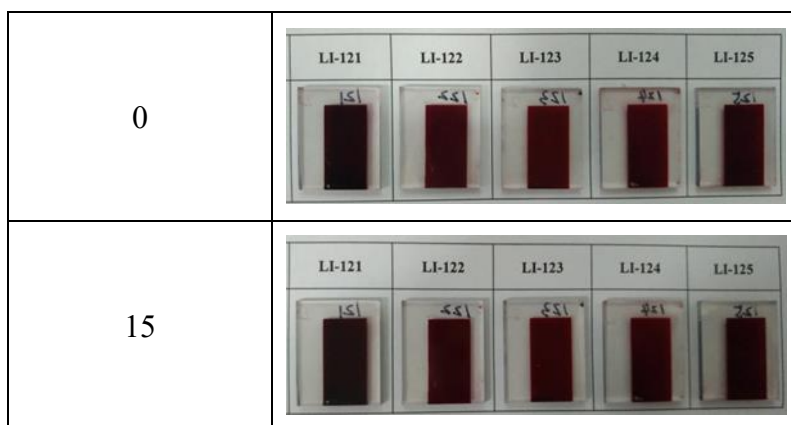


**Figure S11.** The absorption spectra of LI-124 on TiO<sub>2</sub> film after full sun-light irradiation

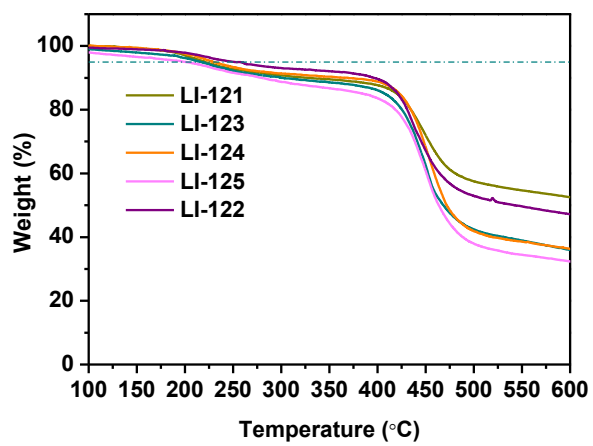


**Figure S12.** The absorption spectra of LI-121-123 and LI-125 on TiO<sub>2</sub> film after full sun-light irradiation

Irradiation time/h	Physiognomy of films
--------------------	----------------------



**Figure S13.** The pictures of dyes on TiO<sub>2</sub> films before and after full sun-light irradiation



**Figure S14.** TGA curves of LI-121-LI-125