### **Energy Materials**

### Enhanced photodegradation of ciprofloxacin with organic photocatalyst through a ternary strategy

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### Materials

PM6 (Poly[[4,8-bis[5-(2-ethylhexyl)-4-fluoro-2-thienyl]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl]-2,5thiophenediyl[5,7-bis(2-ethylhexyl)-4,8-dioxo-4H,8H-benzo[1,2-c:4,5-c']dithiophene-1,3-diyl]-2,5thiophenediyl]).

Y6 (2-[2-[[23-[[1-(dicyanomethylidene)-5,6-difluoro-3-oxoinden-2-ylidene]methyl]-3,27-bis(2-ethylhexyl)-

8,22-di(undecyl)-6,10,15,20,24-pentathia-3,14,16,27-

tetrazaoctacyclo[16.9.0.02,12.04,11.05,9.013,17.019,26.021,25]heptacosa-

1(18),2(12),4(11),5(9),7,13,16,19(26),21(25),22-decaen-7-yl]methylidene]-5,6-difluoro-3-oxoinden-1-ylidene]propanedinitrile).

ITCPTC (3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-cyclopentane-1,3-dione-[c]thiophen))-5,5,11,11tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene).

### Characterization

The morphology images of photocatalysts were obtained from scanning electron microscope (SEM, Zeiss Sigma 300), and elemental mapping was achieved during SEM by energy-dispersive X-ray spectroscopy (EDS). The UV–vis diffuse reflectance spectra were obtained by SHIMADZU UV-2600i & ISR-2600Plus. Photoluminescence (PL) spectra were taken on an Edinburgh Instrument FLS 1000. The Brunauer-Emmett-Teller (BET) calculation was used to investigate the specific surface area (ASAP 2460 3.01 analyzer). The electron spin resonance (ESR) investigations were operated on an ESR spectrometer (ESR, Bruker EMXplus).

Photoelectrochemical measurements of materials were measured using an electrochemical workstation (CHI-660 E, Chenhua, China) with a general three-electrode configuration. Ag/AgCl electrode as the reference electrode, Pt as the counter electrode, the photocatalysts served as the working electrode, and Na<sub>2</sub>SO<sub>4</sub> solution (0.5 M) as the electrolyte. Electrochemical impedance spectroscopy (EIS) was performed over the frequency range of 10<sup>5</sup> Hz to 0.1 Hz. Transient photo-current response test were carried out with an Xe lamp as the light source. The J-V curves were obtained using the SS-F5-3A solar simulator (Enli Technology CO, Ltd.) under AM 1.5G light source.

### Active species trapping experiments

1.0 mM 1,4-benzoquinone (t-BQ), 1.0 mM EDTA-2Na, 1.0 mM IPA were applied for superoxide radical  $(\cdot O_2^-)$ , hole (h<sup>+</sup>) and hydroxyl radical ( $\cdot OH$ ), respectively. Moreover, ESR experiment used 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) as scavengers to determine  $\cdot OH$ ,  $\cdot O_2^-$ radicals and used 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO) as scavengers to determine h<sup>+</sup>.

# Table 1. SEM-EDS element proportion of (A) CSC-PM6: Y6: ITCPTC and (B) CSC-TiO<sub>2</sub>

(A)

Element	Line type	Wt%
С	K-line system	41.20
Ν	K-line system	2.37
0	K-line system	47.53
F	K-line system	1.25
S	K-line system	7.65
(B)		
Element	Line type	Wt%
С	K-line system	66.78
Ti	K-line system	33.22

## Table 2. BET specific surface area and pore diameter of the as-prepared samples

Samples	S <sub>BET</sub> (m <sup>2</sup> /g)	Pore diameter (nm)
CSC	932.5200	2.0754
CSC-PM6: Y6: ITCPTC	894.1811	2.0895

# Table 3. OPV device performance of Y6: ITCPTC

Samples	Voc (V)	J <sub>SC</sub> (mA/cm2)	FF (%)	PCE (%)
1:0	0.593	0.362	0.316	0.068
0.5:0.5	0.739	0.384	0.298	0.084
0:1	0.840	0.506	0.228	0.097

# Table 4. Hole and Electron mobility of PM6: Y6: ITCPTC

Samples	Hole mobility	Electron mobility
1:1:0	0.000591	0.000331
1:0.5:0.5	0.000646	0.000445
1:0:1	0.000581	0.000311

Туре	Model	Equation	Parameters
Adsorption capacity		$q_t = \frac{(C_0 - C_t)V}{m}$	V(L): reaction solution volume, $m(g)$ : the mass of the adsorbent.
Kinetics	pseudo-first- order	$\log (q_{\rm e} - q_{\rm t})$ $= \log q_{\rm e} - \frac{k_1}{2.303}t$	$q_e$ (mg/g): equilibrium adsorption capacity, $q_t$ (mg/g): the sorption amount at time t, $k_l$ (1/min): the adsorption rate constant.
model ps	pseudo- second-order	$\frac{t}{q_{\rm t}} = \frac{t}{q_{\rm e}} + \frac{1}{k_2 q_{\rm e}^2}$	$k_2$ (g/mg·min) : the rate constant determined by the plots of t/qt versus t.
Isotherm	Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$ $R_L = \frac{1}{1 + K_L C_e}$	$q_{\rm e}$ (mg/g): equilibrium adsorption capacity, $C_{\rm e}$ (mg/L): solution equilibrium concentration, $q_{\rm m}$ (mg/g): maximum adsorption capacity, $K_{\rm L}$ (L/mg): Langmuir constant, R <sub>L</sub> : the separation factor.
model	Freundlich	$\ln q_{e} = \frac{1}{n} \ln C_{e} + \ln K_{F}$ $K_{F} = \frac{Q_{m}}{C_{H}^{1/n}}$	$K_{\rm F}$ (L/mg) and <i>n</i> : the Freundlich constants, which represent the adsorption capacity and intensity, C <sub>H</sub> (mg/L): the initial CIP concentration

# Table 5. Detailed information of adsorption capacity and isotherm

# Table 6. Detailed information of Kinetic parameters for CIP adsorption

Comples	Pseudo-first-order model			Pseudo-second-order model	
Samples	$q_{e,exp} (mg/g)$	$q_{e,cal}(mg/g)$	R <sup>2</sup>	$q_{e,cal} (mg/g)$	R <sup>2</sup>
CSC-PM6: Y6: ITCPTC	259.2	270.145	0.9956	336.160	0.9866
CSC	219.2	227.851	0.9970	284.531	0.9902

## Table 7. Summary of photodegradation of CIP reported in recent years

Photocatalyst	Concentration (mg/L)	Time (min)	Efficiency (%)	Reference
Bi/Bi <sub>2</sub> O <sub>3</sub> /TNAs	10	300	90.3	[1]
ZIF-8-derived CuS/ZnO	10	40	94.59	[2]

WSe <sub>2</sub> NPs	10	100	93.4	[3]
TiO <sub>2</sub> / Bi <sub>2</sub> MoO <sub>6</sub> /Ag	10	100	83.58	[4]
BiOCl/BiOIO3	15	60	88	[5]
BiBDC/BiVO <sub>4</sub>	10	60	76.3	[6]
CSC-PM6: Y6: ITCPTC	10	45	97.3	This work

Table 8. The activation energy of different reaction pathways

Pathway	Reaction process	E <sub>a</sub> (kJ/mol)
Ι	CIP→P1	612.356
II	CIP→P5	197.012
III	CIP→P7	536.085



**Figure 1.** SEM images of CSC-PM6: Y6: ITCPTC (a, b), SEM-EDS images of CSC-TiO<sub>2</sub> (c, d, e, f, g), and EDS images of CSC-PM6: Y6: ITCPTC (h).



**Figure 2.** The N<sub>2</sub> adsorption–desorption isotherms and pore size distribution curves of (a) CSC and(b) CSC-PM6: Y6: ITCPTC.



**Figure 3.** Effect of contact time on the adsorption of CIP to the samples under dark conditions, the pseudo-first-order model (a) and the pseudo-second-order model (b) of samples, the Langmuir model (c) and the Freundlich model (d) for CIP adsorption.



Figure 4. Comparison of degradation performance of CIP by different photocatalysts.



Figure 5. Photodegradation of CIP under different catalyst dosages.



Figure 6. (a) TOC and (b) COD removal (%) for CIP degradation.



Figure 7. Photocatalytic degradation of CIP under indoor light irradiation.



Figure 8. (a, b) SEM image of catalyst after degradation.



Figure 9. (a) UV-vis absorption and (b) Raman spectrum of catalyst before and after degradation.



Figure 10. The mass spectrum of the intermediates of CIP.



Figure 11. The Fukui value results of CIP, (a)  $f^-$  and (b)  $f^+$ .



Figure 12. Gibbs free energy of different reaction pathways.



Figure 13. Photodegradation of (a) NOR (10 mg/L) and (b) TC (10 mg/L) under Xe lamp.

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