Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Strong electron affinity PDI supramolecules form anion radicals for the degradation of organic pollutants *via* direct electrophilic attack

Xiaojuan Bai,[a,b] Cong Wang,[a] Xuyu Wang,[a] Tianqi Jia,[a] Boxuan Sun,[a] Shengqi Yang,[a] Di Li,[c] Junqi Li,[a,b] Haiyan Li*[a,b]*

[a]Key Laboratory of Urban Stormwater System and Water Environment (Beijing University of Civil Engineering and Architecture), Ministry of Education

[b]Beijing Engineering Research Center of Sustainable Urban Sewage System Construction and Risk Control, Beijing University of Civil Engineering and Architecture, Beijing 100044, China

[c]School of Chemistry and Chemical Engineering, Xi'an University of Architecture and Technology, Xi'an, 710055, China

E-mail: baixiaojuan@bucea.edu.cn heixia.1986@163.com

Section S1. Details of photoelectrochemical tests

In photoelectrochemical tests, a standard three-electrode cell was used, among which ITO/product sample was used as a working electrode, a platinum wire was used as the counter electrode, and a standard calomel electrode (SCE) as a reference electrode was used in photoelectric investigations, the electrolyte solution was 0.1 M Na_2SO_4 during the tests.

Section S2. Details of theoretical calculation

The solvation model (SMD) implicit model was used with water as solvent.[1] Results involving wavefunction analysis, such as Hirshfeld charge, ALIE and electrostatic potential, were obtained by the Multiwfn program.[2]

1. A. V. Marenich, C. J. Cramer and D. G. Truhlar, *The Journal of Physical Chemistry B*, 2009, **113**, 6378-6396.

2. T. Lu and F. Chen, *Journal of Computational Chemistry*, 2012, **33**, 580-592.

Section S3. Photocatalytic degradation and radical trapping experiments

A multiposition photochemical reactor (1000 W Xe lamp, $\lambda \geq 420$ nm) was used to conduct the photocatalytic degradation experiments. A quartz tube was used as the reactor to perform the photodegradation reactions, which mixed with 25 mg of photocatalyst and 50 mL of MB (5×10^{-5} mol/L) or DCF (5 ppm) solution. Before the light irradiation, the suspensions were ultrasonically dispersed in the dark for 30 min and stirred for 30 min to get the adsorption-desorption equilibrium. At time intervals, 2.5 mL of solution was sampled and centrifuged to remove the photocatalysts. The DCF concentration was determined by high-performance liquid chromatography (HPLC) on an LC-20AT (Shimadzu, Japan) with a UV detector at 275 nm and Roc-C18 (150 mm × 4.6 mm, 5 μm) column, the mobile phase consisted of 0.1% formic acid and acetonitrile (40:60, v/v) at a flow rate of 1.0 mL/min. The MB concentration was analyzed by an ultraviolet-visible spectrophotometer ($\lambda_{max} = 663$ nm). In addition, we performed free radical trapping experiments of DCF under xenon irradiation. Scavengers of each reaction species were added to the reaction solution as described above for the photocatalytic experiments. The concentrations of tert-Butyl Alcohol (*t*BuOH), p-benzoquinone (p-BQ) and EDTA-2Na as scavengers are 5×10^{-4} mol L^{-1}. The pseudo-first-order rate constant for contaminant photocatalytic degradation was obtained by performing a linear regression of the natural log of contaminant concentrations vs time.

Figures

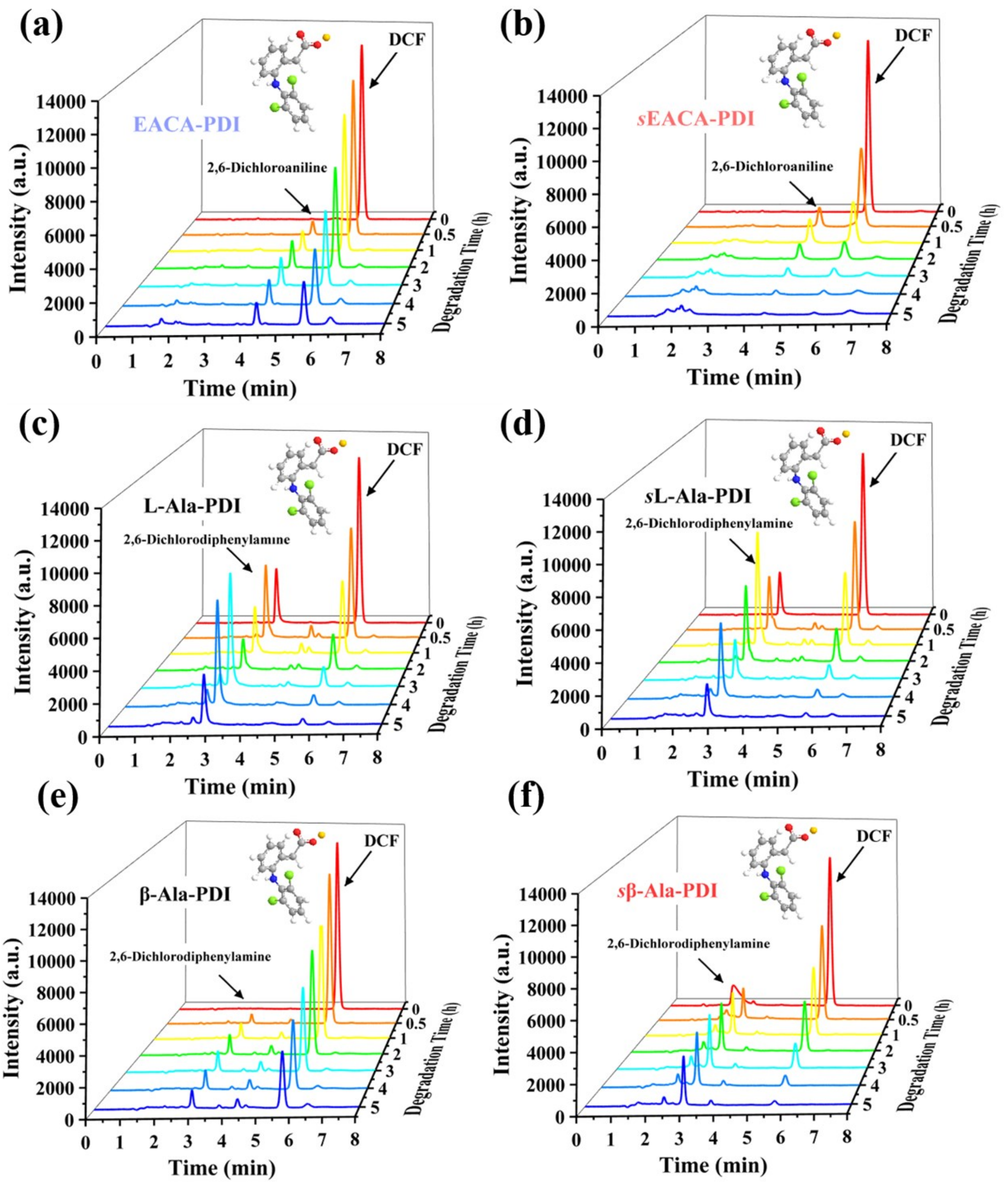

Fig. S1 HPLC diagram of DCF by EACA-PDI (a), *s*EACA-PDI (b), L-Ala-PDI (c), *s*L-Ala-PDI (d), *s*β-Ala-PDI (e), and *s*L-Ala-PDI (f).

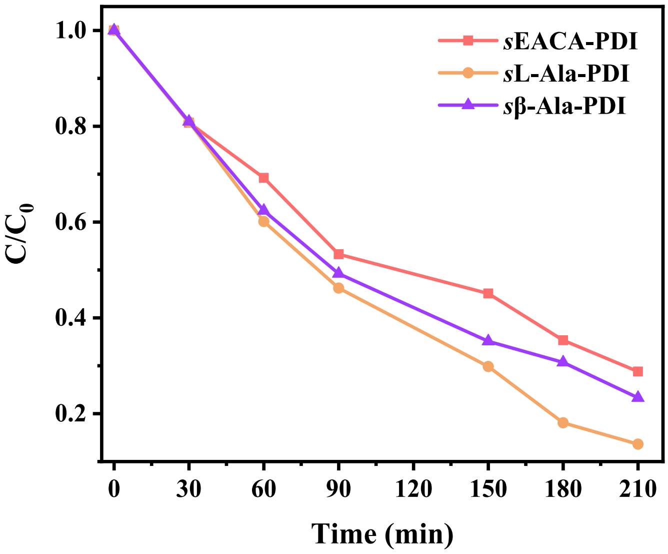

Fig. S2 Degradation trend of MB in photocatalytic process.

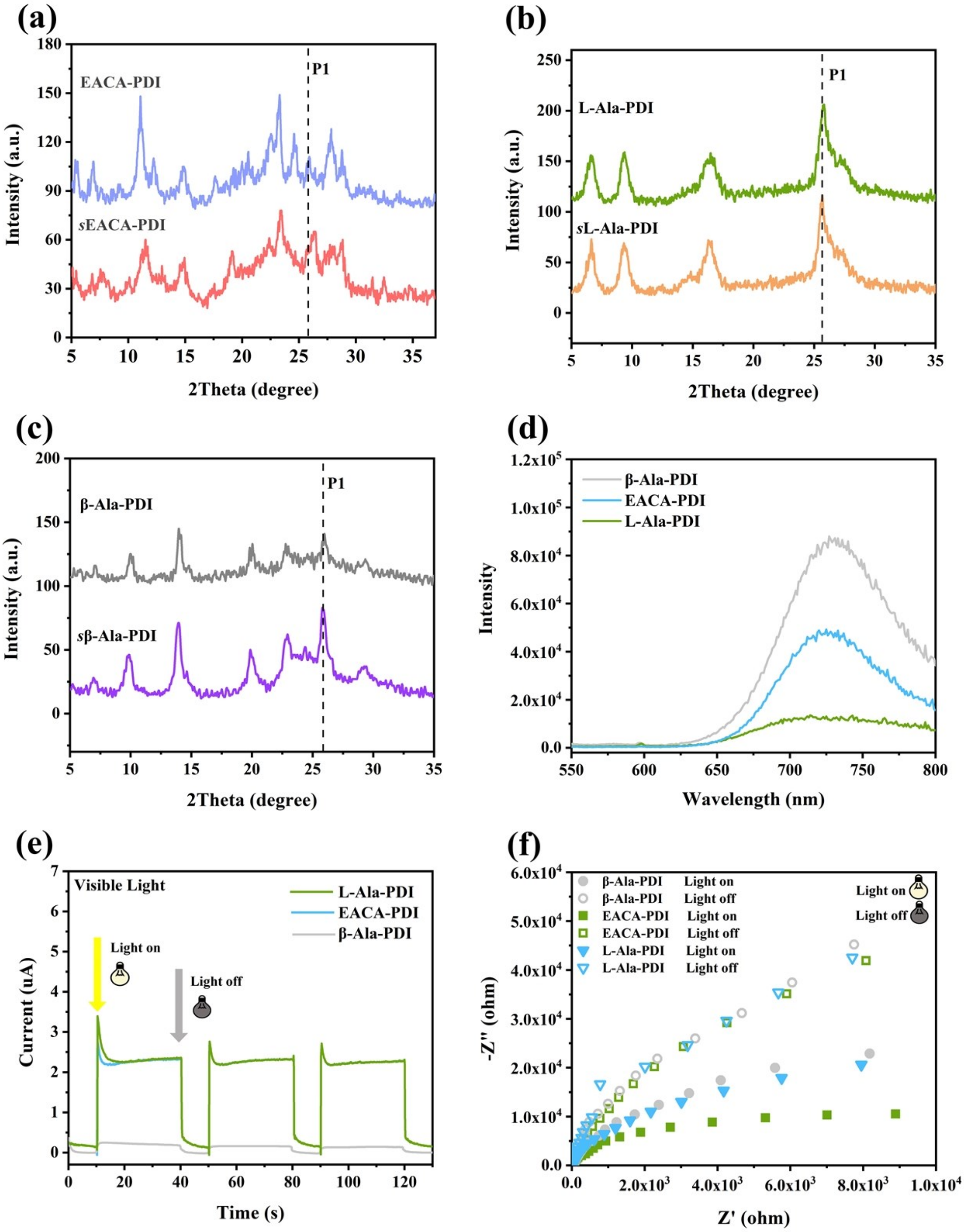

Fig. S3 XRD patterns (a-c) of *s*EACA-PDI, EACA-PDI, *s*L-Ala-PDI, L-Ala-PDI, *s*β-Ala-PDI and β-Ala-PDI. PL spectra (d), photocurrent (e), electrochemical impedance spectroscopy test (f) of EACA-PDI, L-Ala-PDI and β-Ala-PDI.