Asymmetry and Electronic Directionality: A Means to Improving the Red/Near-IR-Light-Responsive Photoactivity of Phthalocyanine-Sensitized Carbon Nitride

Xiaohu Zhang,[a] Lijuan Yu,[a] Renjie Li*,[a] Tianyou Peng* [a] and Xingguo Li[b]

1. Calculation of activation energy

The activation energy of a catalytic reaction can be calculated by the following experimental Arrhenius equation based on rate constant and temperature

$$k = Ae^{-Ea/RT} \qquad (1)$$

Generally, *A* and *Ea* are constant, and represent pre-exponential factor and experimental activation energy respectively. R = 8.314 J mol^{-1} K^{-1} and K represents absolute temperature.

To calculate *A* and *Ea*, the equation (1) is commonly changed as its logarithmic form

$$\lg k = -\frac{Ea}{2.303R} \bullet \frac{1}{T} + \lg A \qquad (2)$$

Therefore, it will be convenient to obtain *A* and *Ea* if two *T* (T_1, T_2) and *k* (k_1, k_2) are known by

$$\lg k_1 = -\frac{Ea}{2.303R} \bullet \frac{1}{T_1} + \lg A \qquad (3)$$

$$\lg k_2 = -\frac{Ea}{2.303R} \bullet \frac{1}{T_2} + \lg A \qquad (4)$$

When (4) – (3), (5) is obtained

$$\lg \frac{k_2}{k_1} = -\frac{Ea}{2.303R} \bullet \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \qquad (5)$$

For the present system, the temperature of the suspension after 1 h irradiation under λ⩾500 nm reaches to ~54 ^oC due to the high intensity of Xe-lamp. However, the he temperature of the suspension after 1 h irradiation under monochromatic light irradiation (λ = 685, 700 or 760 ± 10 nm) can maintain as room temperature (~ 25 ^oC) due to the low transmission light intensity. Generally, the activation energy (*Ea*) for a system is a constant and has nothing to do with reaction conditions. Therefore, it is reasonable to use equation (5) to calculate *Ea* according to the two reaction rates and temperatures under λ⩾500 nm and monochromatic light irradiation respectively. Take Zn-*tri*-PcNc-2-Pt/g-C_3N_4 as example, the k_1 = 173.3 μmol/h (which is obtained by the linear fitting of first 10 h of Figure 5) and T_1 = 327 K under λ⩾500 nm, and the k_2 = 27.7 μmol/h and T_2 = 298 K under λ = 700 ± 10 nm. Therefore, the activation energy (*Ea*) for Zn-*tri*-PcNc-2-Pt/g-C_3N_4 is 50.72 kJ/mol. Accordingly, the activation energy (*Ea*) for the six system of Zn-*tri*-PcNc-2-Pt/g-C_3N_4, Zn-*tri*-PcNc-1-Pt/g-C_3N_4, Zn-*tri*-PcNc-3-Pt/g-C_3N_4, Zn-*tetrad*-Nc-3- Pt/g-C_3N_4, Zn-*tetrad*-Pc-1- Pt/g-C_3N_4 and Zn-*tetrad*-Pc-2- Pt/g-C_3N_4 are 50.72, 41.63, 58.50, 69.81, 38.73 and 88.06 kJ/mol respectively.

2. EIS analysis

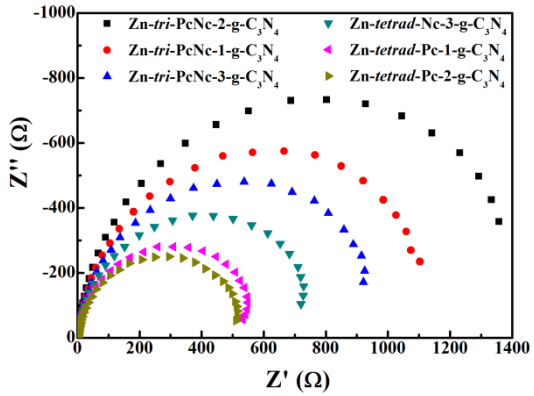

Figure S1. EIS spectra of the six dyes sensitized g-C_3N_4.

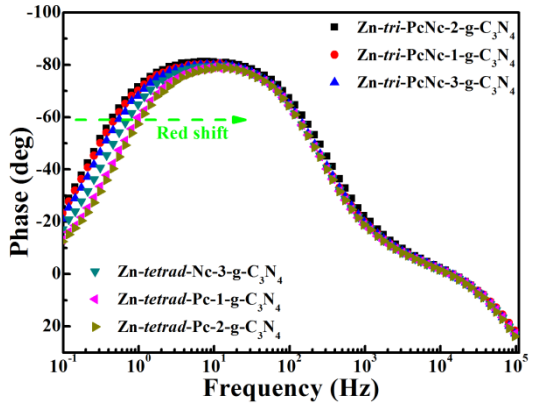

Figure S2. Bode plots of the six dyes sensitized g-C_3N_4.

Table S1. Photoelectrochemical Data of the six dyes sensitized g-C_3N_4.

system	R_2 (Ω)	f (Hz)	τ_n (ms)
Zn-*tri*-PcNc-2-g-C_3N_4	1573	5.486	28.9
Zn-*tri*-PcNc-1-g-C_3N_4	1235	6.643	23.9
Zn-*tri*-PcNc-3-g-C_3N_4	1030	8.071	19.7
Zn-*tetrad*-Nc-3-g-C_3N_4	800	9.766	16.3
Zn-*tetrad*-Pc-1-g-C_3N_4	593.5	11.91	13.4
Zn-*tetrad*-Pc-2-g-C_3N_4	542.7	14.36	11.1