Supporting Information

An 'ice-melting' kinetic control strategy for highly photocatalytic organic nanocrystals

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S1. Calculation of the release rate for $2-H_2TPyP$ molecules

To determine the release rate of 2-H₂TPyP molecules during the ice-melting process, several assumptions were made, i.e., a constant release speed at the same time interval (5 min), cube-shaped ice and a fast reaction speed between acidic 2-H₂TPyP solution (Solution A) and basic surfactant solution (Solution B).

The number of 2-H₂TPyP molecules released per time was calculated based on the concentration of Solution A (0.01 M), and the melted volume (V) and melting time were the key variables. For example, Solution A was frozen and melted in Solution B. The number of 2-H₂TPyP molecules per volume (μ) was 6.02×10¹⁸ based on the following equation:

$$\mu = N_A c (1)$$

where c is the concentration of Solution A (0.01 M), N_A is Avogadro's constant (6.02×10^{23}), indicating that there are approximately 6.02×10^{18} 2-H₂TPyP molecules per milliliter.

The melted volume (mL) of frozen Solution A as a function of time (min) was also measured (Fig. 1). The curve of the melted volume versus time was fitted as a polynomial function, which was described by the following equation:

$$y = 1.858 \times 10^{-4} x^{2} + 0.013 x - 0.135$$
 (2)

Equation (2) gave the relation between the released rate and time. Based on (2) we can estimate that the average number of released molecules (v) was 2.2×10^{15} per second, as described by the following equation:

$$v = \frac{\mu \int_{0}^{50} y' dx}{3000} (3)$$

In comparison, in a conventional method with Solution A and Solution B, the moment (t) that Solution A was dropped into Solution B is significantly short (t << 1 millisecond); in this case we assumed 1×10^{-2} second. As a result, the number of 2-H₂TPyP molecules released per second was 6.02×10^{20} when using a conventional method.

S2. Structural analysis of 2-H₂TPyP and 2-ZnTPyP nanostructures

Upon ice-melting, the acidic 2-H₂TPyP or 2-ZnTPyP molecules (protonated) were released into the base solution, which triggered the acid-base neutralization reaction. Then, deprotonation of acidic porphyrin took place and subsequently slow self-assembly, to finally yield the precipitates. It takes about 50 min for the frozen 2-H₂TPyP or 2-ZnTPyP to completely melt in the base solution at 0 °C. We then collected the precipitates by centrifugation for characterization of structure and properties at time intervals of 5, 15 and 25 min, respectively.



Fig. S1. SEM and TEM images of SDS-assisted 2-H₂TPyP under different methods: (A, B) Ice-melting 5 min, (C, D) Ice-melting 15 min, (E, F) Ice-melting 25 min, (G, H) Conventional 5 min, (I, J) Conventional 15 min, (K, L) Conventional 25 min.



Fig. S2. XRD spectra of SDS-assisted 2-H₂TPyP samples under different methods.



Fig. S3. SEM and TEM images of SDS-assisted 2-ZnTPyP under different methods: (A, B) Ice-melting 5 min, (C, D) Ice-melting 15 min, (E, F) Ice-melting 25 min, (G, H) Conventional 5 min, (I, J) Conventional 15 min, (K, L) Conventional 25 min.



Fig. S4. XRD spectra of SDS-assisted 2-ZnTPyP samples under different methods.



Fig. S5. TEM images and SAED patterns of CTAB-assisted 2-ZnTPyP under different methods: ice-melting 15 min (A, B) and conventional 15 min (C, D).



Fig. S6. (A) Nitrogen adsorption-desorption isotherms and (B) pore size distributions of the SDS-assisted 2-H₂TPyP and 2-ZnTPyP sampled under different methods (15 min).

S3. Computational analysis of 2-ZnTPyP self-assembly



Fig. S7. The atomic structure models of 2-ZnTPyP dimer with 10 H₂O molecules (A, B), and with 22 H₂O molecules (D, E); (C) and (F) are the corresponding electron density difference distribution during AIMD simulations.

To study the interaction nature of the 2-ZnTPyP dimer in aqueous solution, the difference electron density $\rho(\mathbf{r})$ was also analyzed. Here $\Delta\rho(\mathbf{r})$ was obtained by subtracting the electron densities of non-interacting 2-ZnTPyP monomer component systems, from the density $\rho(\mathbf{r})$ of the formed 2-ZnTPyP dimer, while retaining the atomic positions of the component systems at the same location as in the 2-ZnTPyP dimer. As shown in Fig. S7C and S7F, red and black lines represent charge depletion and accumulation, respectively. Large charge change between Zn₂ and pyridine C at the neighboring porphyrin could be gained for the 2-ZnTPyP dimer in the environment of 10 or 22 H₂O molecules.



Fig. S8. Pair-correlation functions of Zn and C with difference studied conditions during AIMD simulations.

The pair-correlation functions (PCFs) g(r) defined the possibility of finding a particle at a distance *r* from a given atom,

$$g(r) = \frac{1 \quad dn(r,r+dr)}{<\rho > dv(r,r+dr)} (4)$$

Herein, dn(r, r + dr) represented the number of particles in the interlayer volume of the thin spherical shell dv(r, r + dr), of which r and dr were the radius and the microscale thickness respectively. $< \rho >$ stood for the average particle number density of the system. In Fig. S8, the peak of g(r)_{Zn-C} exited at about 3.08 Å, in good agreement with the distance between Zn and benzene ring C in the porphyrin molecule. The peak of Zn-C PCF $g(r)_{Zn-C}$ around 2.14 Å occurred in 2-ZnTPyP dimer, but disappeared in the 2-ZnTPyP monomer, indicating that this peak corresponds to the distance between Zn and pyridine C at the neighboring porphyrin molecule.

S4. XRD characterization of representative Alq3 nanostructures



Fig. S9. XRD spectra of the representative Alq3 samples. The shift of the XRD peaks to large θ indicated the narrowed interplanar spacing.

S5. Photoelectronic properties and photocatalytic performance of 2-ZnTPyP nanostructures

The tests on the photoelectronic properties and photocatalytic performance were mainly performed on the SDS-assisted 2-ZnTPyP samples under different methods.



Fig. S10. Raman spectra of 2-ZnTPyP samples under different methods.

Table S1. The carrier lifetime of 2-ZnTPyP under different methods in time-resolved fluorescence.

Sample	$\tau_1(ns)$	B_{I}	$\tau_2(ns)$	<i>B</i> ₂	$<\tau>^a(ns)$
2-ZnTPyP (conventional 15 min)	0.67	566.66	3.13	101.05	1.79
2-ZnTPyP (ice-melting 15 min)	0.62	549.37	1.82	61	0.91
$a < \tau > = (B_1 \tau_1^2 + B_2 \tau_2^2)/(B_1 \tau_1 + B_2 \tau_2)$					



Fig. S11. Photocurrent densities of 2-ZnTPyP samples under different methods.



Fig. S12. Catalytic efficiencies of 2-ZnTPyP samples under different methods.



Fig. S13. XRD spectra of of the ice-melting 2-ZnTPyP samples after eight repeated runs of MB degradation.