Electronic supplementary information (ESI) for

In situ observation of heterogeneous catalytic organic reactions via aggregation-induced emission luminogens

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Supplementary Text

Materials and instrumentation

All commercially available chemicals and regents used as received without further purification. The molecular probe (TPEMI-DA) was synthesized and characterized according to our previous report.[1] ^{1}H and ^{13}C NMR spectra were measured on a JEOL JNM-ECA400 (400 MHz) spectrometer in DMSO-d_6 or chloroform-d using tetramethylsilane as internal reference. The fluorescence spectra were measured by a fluorescent photometer (SHIMADZU RF2000). The fluorescent images were recorded with either a digital single-lens reflex camera or a smart phone.

Synthesis of maleimides OMeMI

Briefly, amines were dissolved in polar aprotic solvents (such as acetonitrile and tetrahydrofuran) at a concentration of about 1 millimole per mililitre (mmol/mL). And a solution of maleic anhydride in dichloromethane (1 mmol/mL) was added dropwised at room temperature. The mixture was stirred at room temperature for 12 hours. During this process, a light yellow precipitate forms, which was collected and washed by dichloromethane. After drying, the precipitate was transferred into a flask together with acetic anhydride (5 mL per 1 g of the precipitate) and sodium acetate (0.5 g per 1 g of the precipitate). The mixture was heated at 80 ^{o}C for 4 hours under nitrogen protection, and poured into ice water after cooling down. The light yellow precipitate was collected, washed with water, dried, and characterized by NMR spectra (Figure S8).

Synthesis of maleimide-furan adducts (OMeMI-DA)

Maleimide-furan adducts was synthesized by mixing the OMeMI and 2,5-dimethylfuran in dichloromethane, and stirred at 25-30 ^{o}C for 12 hours. The product was purified by recrystallization and characterized by NMR spectra (Figure S9).

Quantitative relationship between brightness and area density of TPEMI-DA

To establish the quantitative relationship between the area density of TPEMI-DA coated on the particles and the brightness of the particles coated with TPEMI-DA, we carefully transferred a serious controlled amount of TPEMI-DA on the silica plates, and acquired the fluorescent image (Figure S2a). The digital values of the brightness were extracted from the image, and plotted against the amount of TPEMI-DA (Figure S2b). According to the linear fitting, below a threshold brightness of approximately 60%, there is a linear relationship between brightness and the quantity of TPEMI-DA per unit area:

$$\mathrm{B} = 57 \times \mathrm{AD} + 1$$

where B is brightness of the spot, and AD is the area density of TPEMI-DA.

Estimation of the thickness of reporters coated on the particles

To estimate the thickness of the fluorescent reporters coated on the particles, we assume that the molecules form uniform layer on the surfaces, and calculate the thickness of the organic coating (h) to be 0.07 nm using the following equation:

$$h = \frac{m_{reporter}/\rho_{reporter}}{M_{particles} \times S_{particles}}$$

where four parameters is involved:

$m_{reporter}$: the mass of molecular probes transferred to the particles (0.35 μg), which is estimated based on the concentration of the probes (the typical value is 1.0 mg/mL) and the volume of liquid that transferred from the capillary tubes to the particles (about 0.35 mm^3);

$\rho_{reporter}$:the density of molecular probes (about 1 g/cm^3);

$M_{particles}$: the mass of particles in each spot of catalysts (about 5 mg);

$S_{particles}$: the surface area of catalysts. As the size of the particles range from several tens nanometers to several micrometers, their surface area should be lager than 1 m^2/g.

An average thickness of 0.07nm means that, assuming the molecular size as 1.0 nm and monolayer deposition, the probes can only cover 7% of the surface. Therefore, it is unlikely that the probes form multilayers on the surface.

Preparation of samples for screening catalysts at solid-gas interface

The particles were dispersed in water at a solid content of 10-30%. One drop of each dispersion was transferred onto a glass plate and dried in an oven. The solution of TPEMI-DA or TPEMI (the concentration is about 1 mg/mL in ethyl acetate) was transferred to the particles using commercial-available capillary tubes, and dried in air.

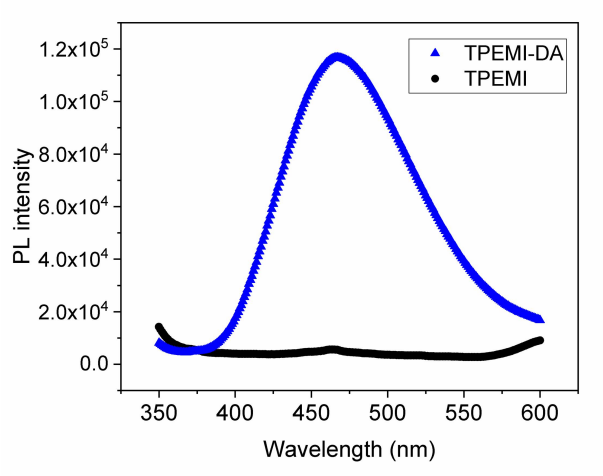

Figure S1. The photoluminescence (PL) spectra of TPEMI-DA and TPEMI taken under 320 nm excitation at a concentration of 100 μM.

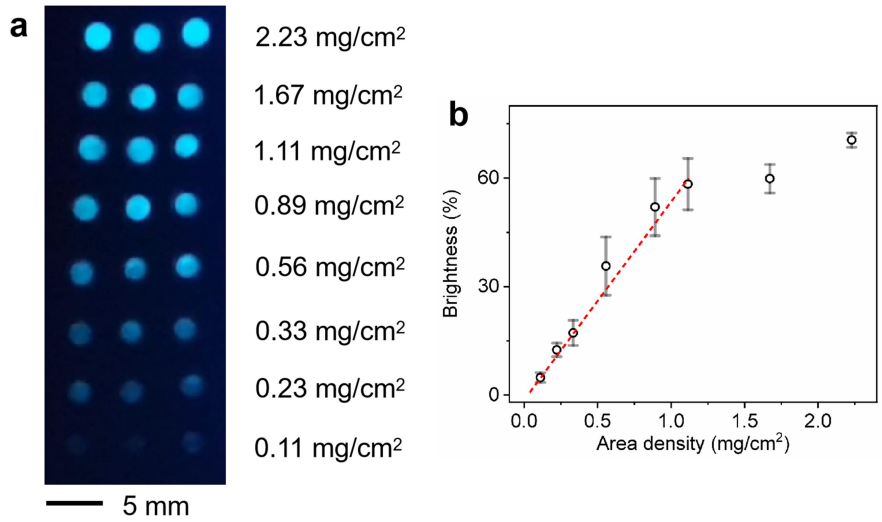

Figure S2. Relationship between brightness of fluorescent image and the area density (AD) of TPEMI-DA. (**a**) Fluorescent image of sample with different AD of TPEMI-DA. (**b**) Plots of brightness against the AD of TPEMI-DA.

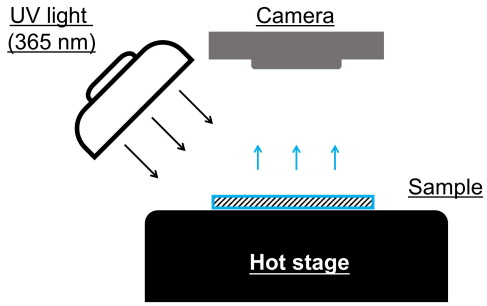

Figure S3. Illustration of the set-up for recording fluorescent evolution during rDA reaction of TPEMI-DA on the surface of silica plates.

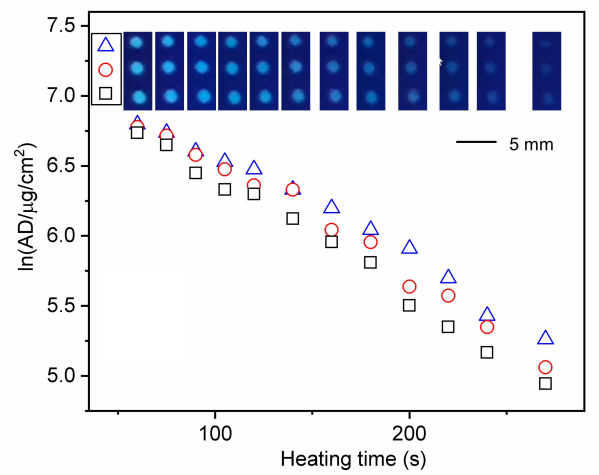

Figure S4. Fluorescent turn-off of TPEMI-DA on silica when heated at 79 °C. The digital values of AD for plotting were acquired based on the brightness values from the inserted fluorescent images. Rate constants were obtained directly from the minus of the slope by linear fit of the curves.

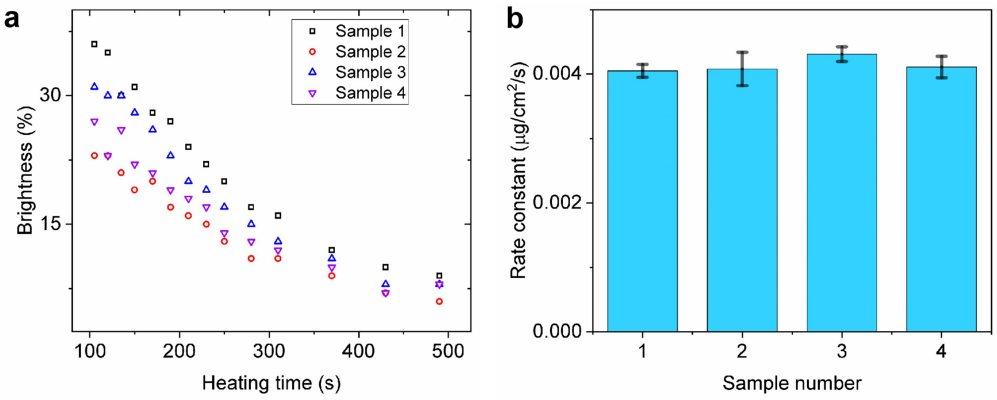

Figure S5. (**a**) Fluorescent evolution on silica coated with different quantities of TPEMI-DA heated at 70 °C. (**b**) Reaction rate constants extracted from the fluorescent evolution. The error bars represent the standard deviation in the linear fitting.

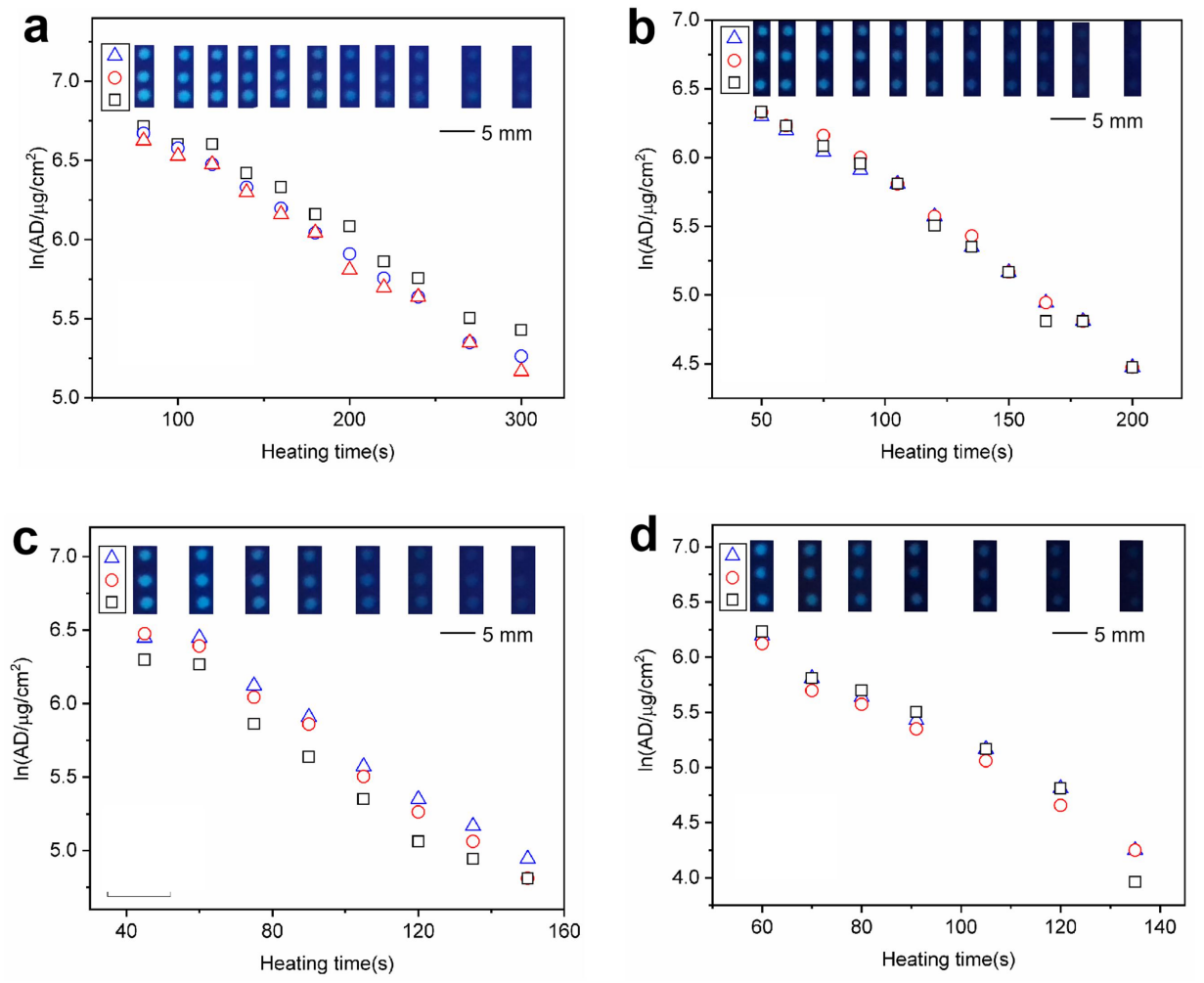

Figure S6. Fluorescent evolution of TPEMI-DA on silica when heated at 76 ºC (**a**), 83 ºC (**b**), 87 ºC (**c**), and 90 ºC (**d**), respectively.

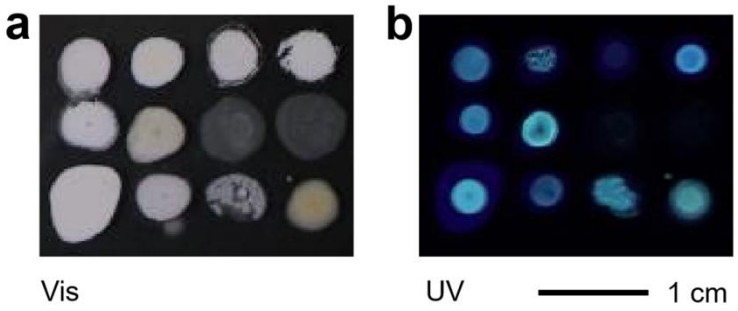

Figure S7. Optical (**a**) and fluorescent (**b**) images after fuming the sample in Fig. 3b with 2,5-dimethylfuran for 1h. Fluorescence on the catalysts was recovered by different magnitude depending on their difference in catalytic activities, which reflects their difference in the catalytic activity to DA reaction.

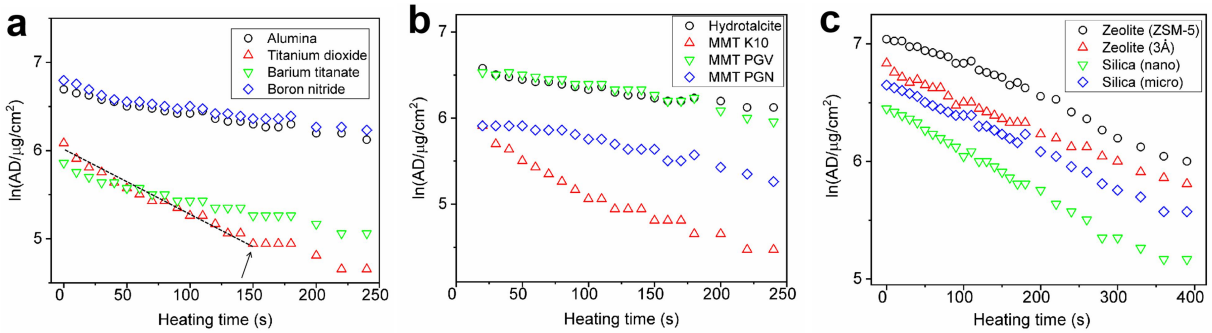

Figure S8. Kinetics traces of the rDA reaction on different catalysts at 70 °C. The digital values of AD for plotting were acquired from the sample presented in Fig. 3. For curves that deviate from the straight line (such as the curve indicated by the arrow in a), only the interval close to linear was selected in linear fitting.

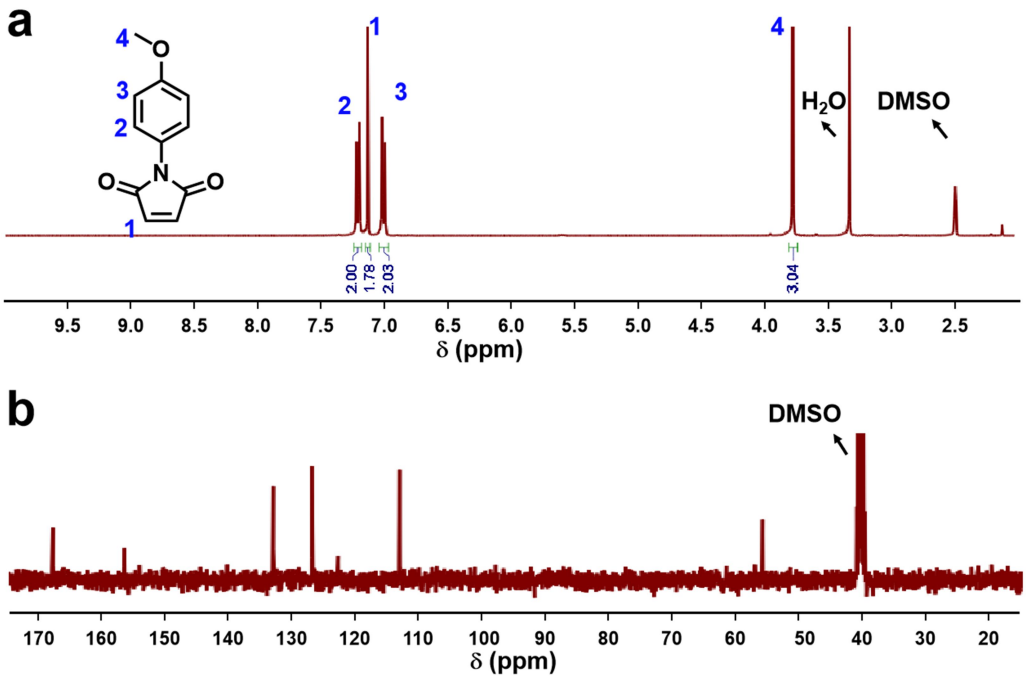

Figure S9. ^{1}H and ^{13}C NMR spectra of OMeMI in DMSO-d_6 with corresponding assignments.

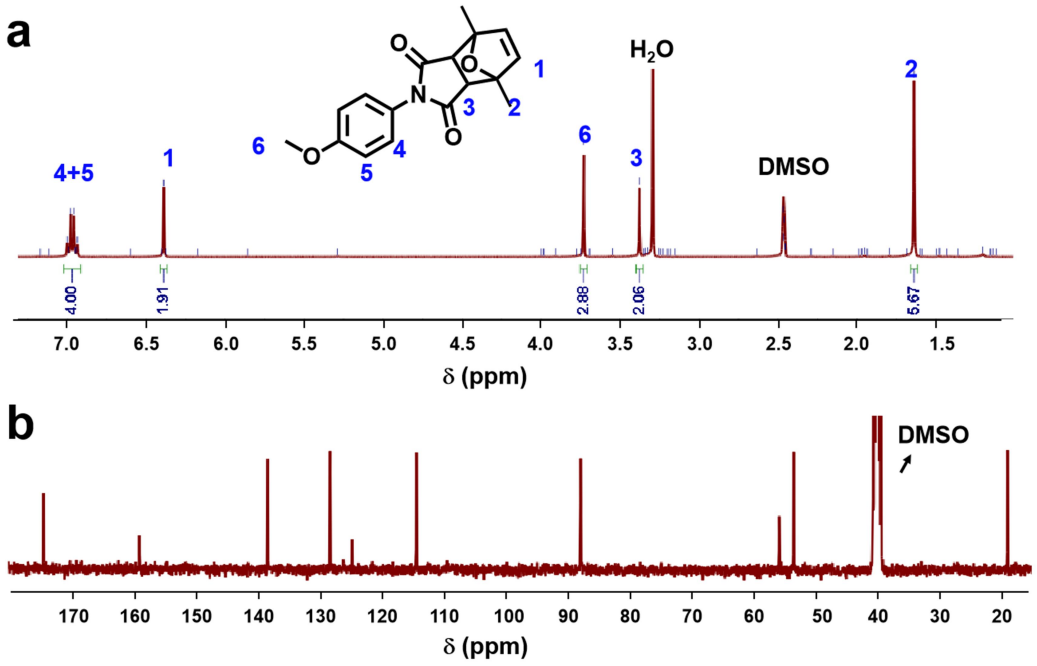

Figure S10. ^{1}H and ^{13}C NMR spectra of OMeMI-DA in DMSO-d_6 with corresponding assignments. .

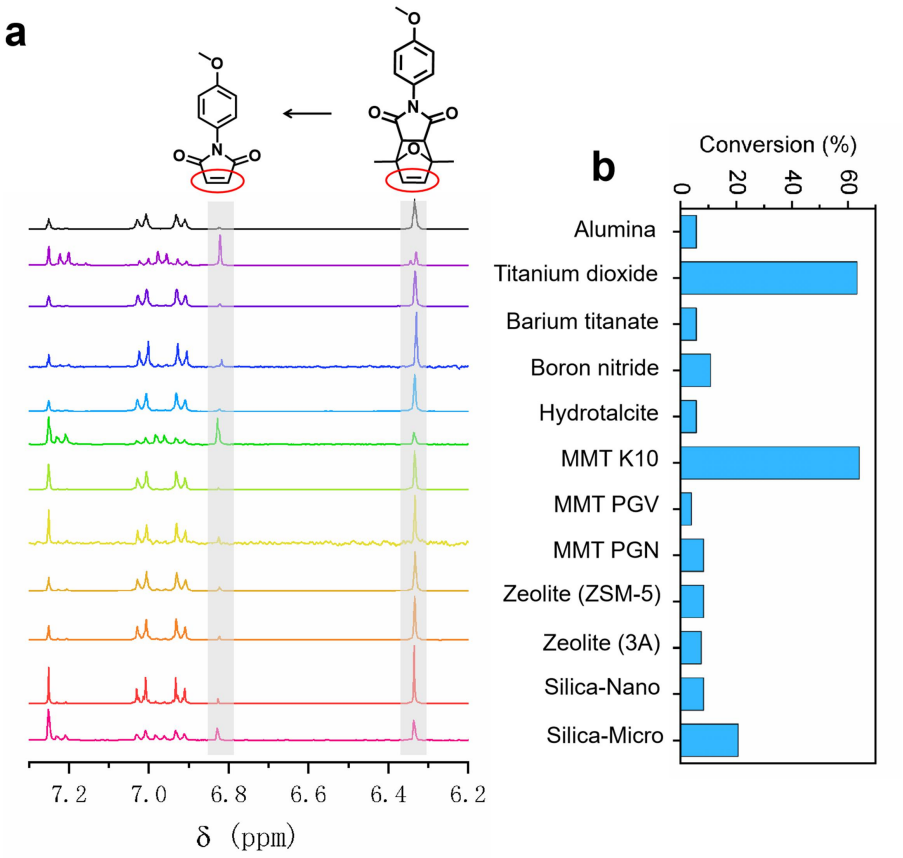

Figure S11. ^{1}H NMR qualitatively reproduces the results in catalysts screening by AIEgens. (**a**) The ^{1}H NMR spectra (chloroform-d) of crude products in the model reaction catalyzed by different catalysts. OMeMI-DA was coated on the catalysts, and heated at 70 °C for 4 minutes. The crude products were then extracted by dichloromethane and ethyl acetate. After the solvents were removed, the residues was dissolved in chloroform-d_3 and subjected to ^{1}H NMR characterization. (**b**) Reaction conversion calculated from the NMR results. The conversion was calculated based on the integration of peaks at 6.83 ppm and 6.34 ppm, which correspond to the product (OMeMI) and the reactant (OMeMI-DA), respectively.

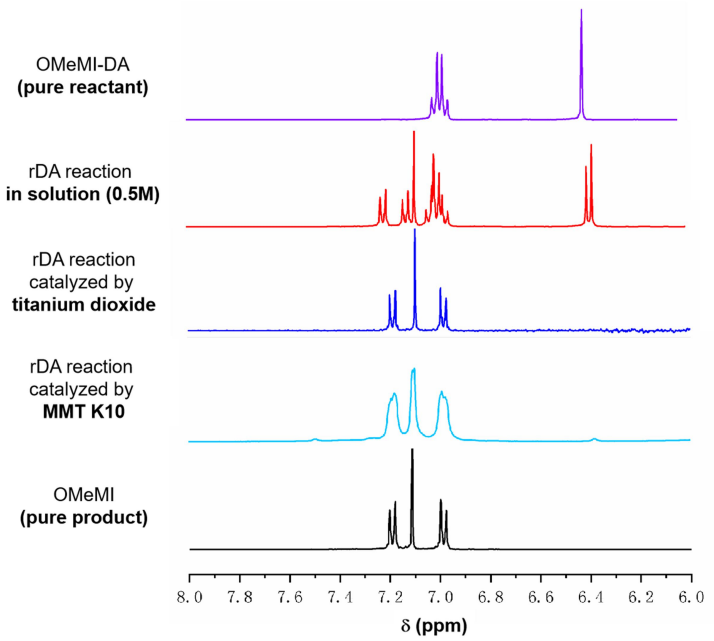

Figure S12. ^{1}H NMR characterization (in DMSO-d_6) of OMeMI-DA decomposed in different conditions at 90 °C. In a DMSO solution (0.5M) without catalysts, heating for 10 minute results in40% conversion, along with 20% isomerization. In contrast, reaction was completed within 10 minutes on the surface of titanium dioxide and MMT K10.

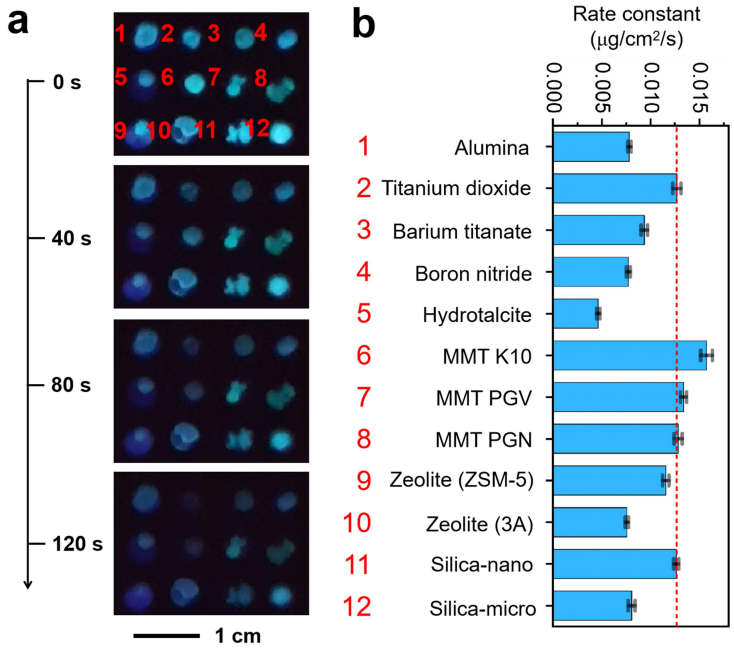

Figure S13. rDA reaction of TPEMI-DA on the surfaces of different catalysts at 85 °C. (**a**) Evolution of fluorescence. (**b**) Rate constants of the reaction on different catalysts. The error bars represent the standard errors in linear fitting.

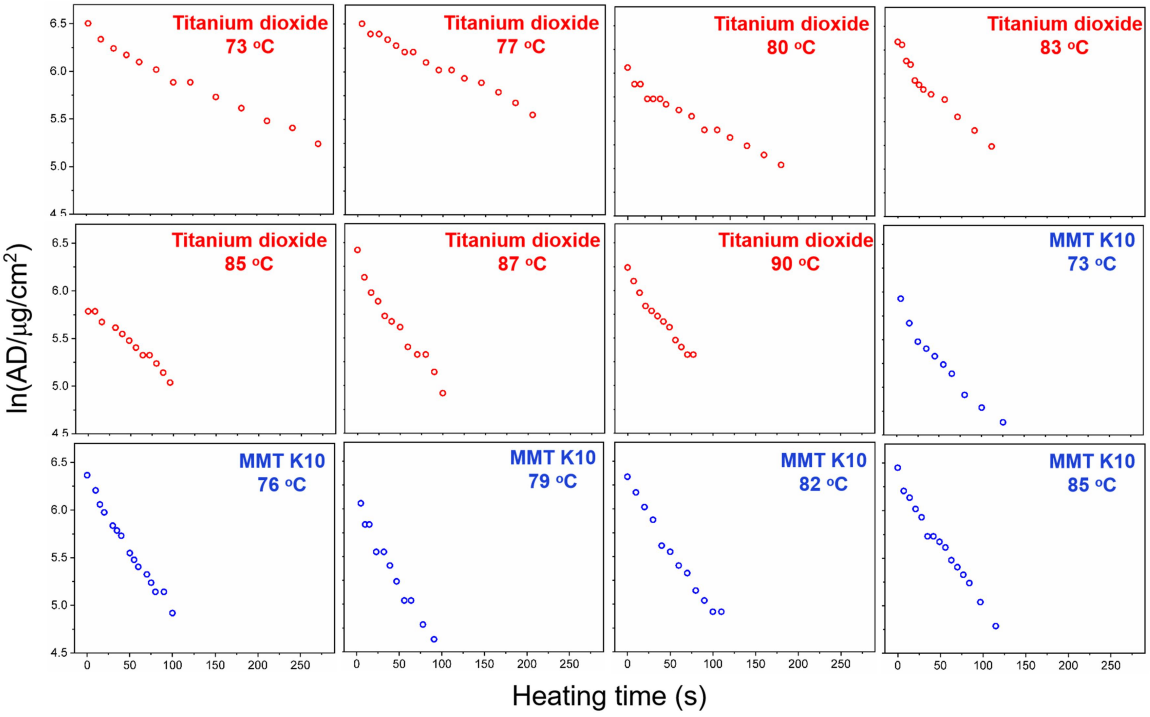

Figure S14. Representative fluorescent evolution during rDA reaction of TPEMI-DA deposited on titanium dioxide (red circle) and MMT K10 (blue circle) and heated at different temperatures.

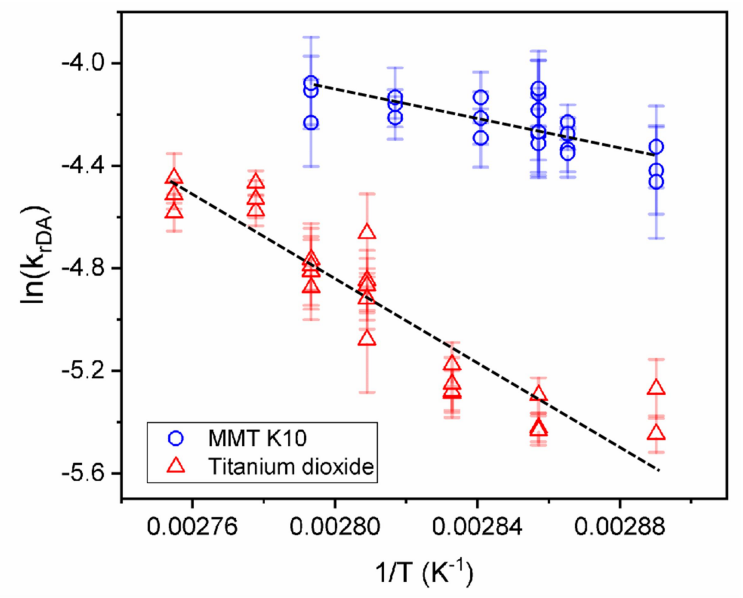

Figure S15. The Arrhenius plots of rDA reaction of TPEMI-DA catalyzed by titanium dioxide (red triangle) and MMT K10 (blue circle). The dashed lines are mark of linear fitting. The error bars represent the standard deviation of the linear fitting.

Reference

1. J. Ji, D. Hu, J. Yuan and Y. Wei, *Adv. Mater.*, 2020, **32**, 2004616.