

Supplementary Information

**Chemical Fuel-Driven Transient 2D Supramolecular Organic
Frameworks (SOFs): Catalysis for Green Synthesis**

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1. General information

1.1. Materials

All chemicals were commercially available and used without further purification.

1.2. Instruments.

Nuclear magnetic resonance (NMR) spectroscopy. ^1H -NMR spectra and were recorded on a JNM-ECZ400S/L1 400MHz NMR spectrometer. Deuterated dimethyl sulfoxide (DMSO-d_6), deuterated chloroform (CDCl_3) and deuterium oxide (D_2O) were used as solvents.

Ultraviolet and visible (UV-vis) spectrophotometry. UV-vis spectra was performed by a SHIMADZU UV1900 UV spectrophotometer.

Dynamic light scattering (DLS). DLS was carried out by a Malvern Zetasizer (Nano ZS90).

Electron paramagnetic resonance. EPR spectra were obtained using MS-5000X spectrometer.

Transmission Electron Microscope (TEM). TEM images were recorded on JEM-F200, JEOL Ltd., Japan.

Scanning electron microscope (SEM). SEM images were recorded on JSM-7610F, JEOL Ltd., Japan.

Atomic force microscope (AFM). AFM images were recorded on SPM-9700HT, Shimadzu Ltd., Japan.

All tests were performed at 25 °C.

2. Procedure of test

Time-dependent photos. Smart phone was put on flat table. Firstly, we took a photo of TPE-4MV²⁺-Me (0.04mM) and CB[8] (0.08mM) mixed aqueous solution (2 mL) in quartz cell. Then we add SDT (2.4 mM) and recorded time-dependent video until the color of mixed system back oxidized state.

Nuclear magnetic resonance (NMR) spectroscopy. Appropriate sample were dissolved in deuterated solvent to conduct NMR test.

UV-vis spectroscopy. Firstly, we took TPE-4MV²⁺-Me (0.04mM) and CB[8] (0.08mM) mixed aqueous solution (2 mL) in quartz cell to conduct UV-vis test. Then we add SDT (2.4 mM) until the spectrogram of mixed system overlapped with oxidized state.

Dynamic light scattering (DLS). Firstly, we took TPE-4MV²⁺-Me (0.04mM) and CB[8] (0.08mM) mixed aqueous solution (2 mL) in polystyrene cell to conduct DLS test. Then we add SDT (2.4 mM) until the species population of mixed system overlapped with oxidized state.

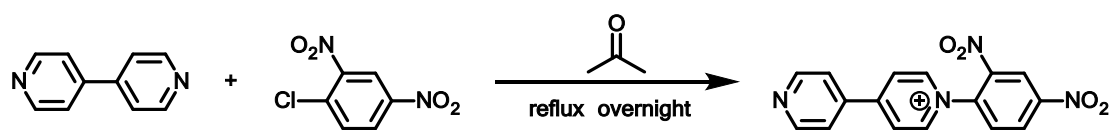
Electron paramagnetic resonance. Firstly, we took TPE-4MV²⁺-Me (0.04mM) and CB[8] (0.08mM) mixed aqueous solution (2 mL) in capillary to conduct EPR test. Then we add SDT (2.4 mM) until the spectrogram of mixed system overlapped with oxidized state.

Transmission Electron Microscope (TEM). 10 μ L sample was dropped on copper grid under high vacuum for 30 min before TEM test.

Scanning electron microscope (SEM). 10 μ L sample was dropped on silicon wafer under high vacuum for 30 min before SEM test.

Atomic force microscope (AFM). 10 μ L sample was dropped on silicon wafer under high vacuum for 30 min before AMF test.

3. Synthesis of TPE-4MV²⁺-Me¹



Scheme 1 Synthesis of 1-(2,4-dinitrophenyl)-4-phenylpyridinium

4,4'-bipyridine (2.02 g, 10 mmol) and 2,4-Dinitrochlorobenzene (1.56 g, 10 mmol) were dissolved in acetone, the solution was stirred at 75 °C overnight under reflux. After the reaction completed, the filter cake was washed by ether and dried under vacuum to afford a gray solid. The corresponding yield was 83%. ¹H-NMR (400 MHz, DMSO-d₆) δ 7.11 (d, 1H), 6.99–6.95 (m, 2H), 6.66 (dd, 1H), 6.57–6.53 (m, 2H), 6.43–6.38 (m, 2H), 5.99 (d, 1H), 5.74 (dd, 2H). LC-MS (ESI): m/z [M-Cl]⁺ calculated for C₁₆H₁₁N₄O₄: 323.29; found: 323.18.

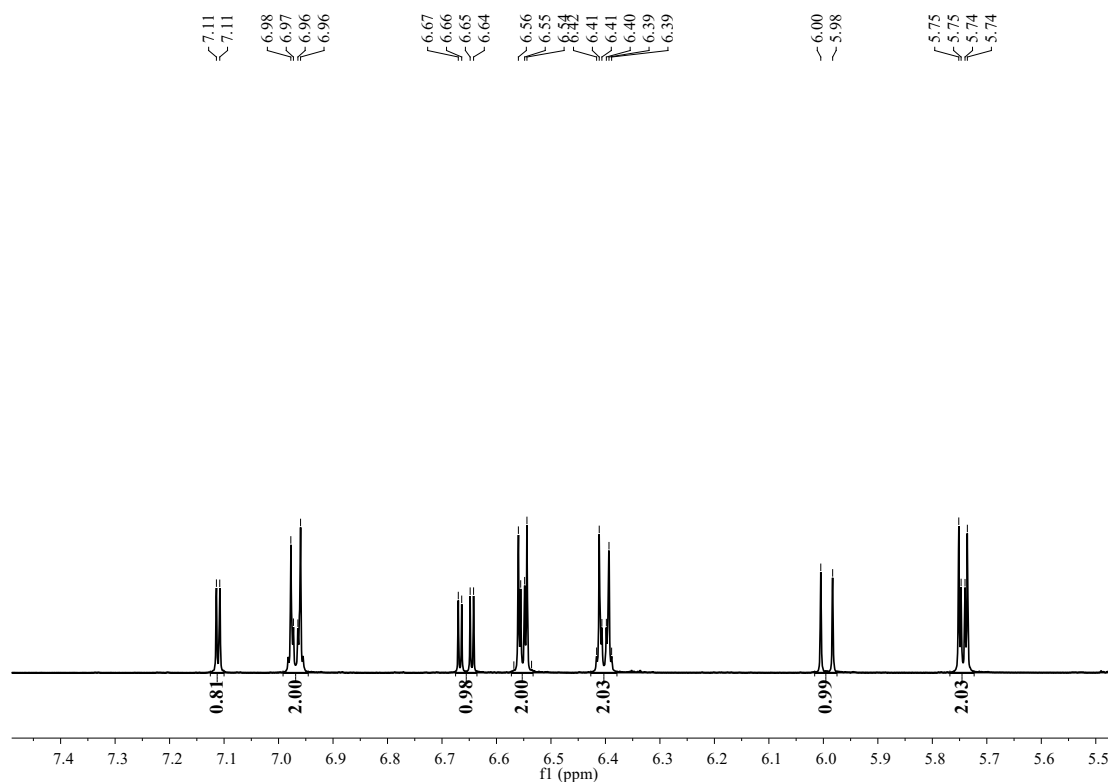
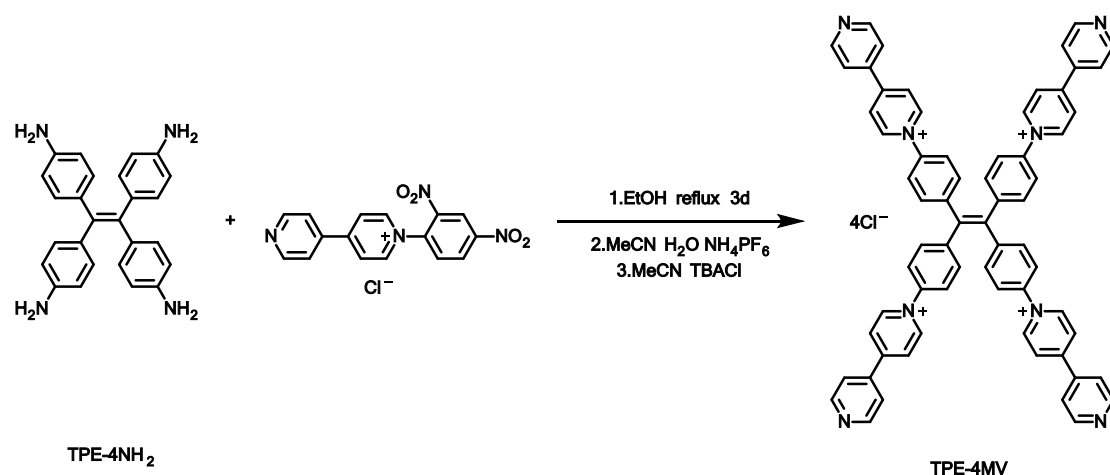


Fig. S1 ¹H-NMR of 1-(2,4-dinitrophenyl)-4-phenylpyridinium



Scheme 2 Synthesis of TPE-4MV

TPE-4NH₂ (0.5 g, 1.27 mmol) and 1-(2,4-dinitrophenyl)-4-phenylpyridinium (3.6 g, 10 mmol) were dissolved in anhydrous ethanol and reacted under reflux for 3 days. After reaction completed, the mixture was cooled to room temperature and ethanol was removed by distillation under reduced pressure, then the solid was collected by filtering with the addition of acetonitrile. The filter cake was dissolved in saturated ammonium hexafluorophosphate (NH₄PF₆) solution and the filter cake was collected dried under vacuum to afford yellow solid. The dried solid was dissolved in MeCN, tetrabutylammonium chloride (TBACl) was added, and then the resulting mixture was filtered. The collected filter cake was dried under vacuum to obtain the orange solid. The corresponding yield was 86%. ¹H-NMR (400 MHz, DMSO-*d*₆) δ 9.65 – 9.59 (m, 8H), 9.49 (dd, 8H), 9.12 – 9.05 (m, 8H), 8.79 – 8.74 (m, 8H), 8.28 – 8.21 (m, 8H), 8.16 – 8.09 (m, 8H). LC-MS (ESI): *m/z* [M-4Cl]⁴⁺ calculated for C₆₆H₄₈N₄: 238.10; found: 238.22.

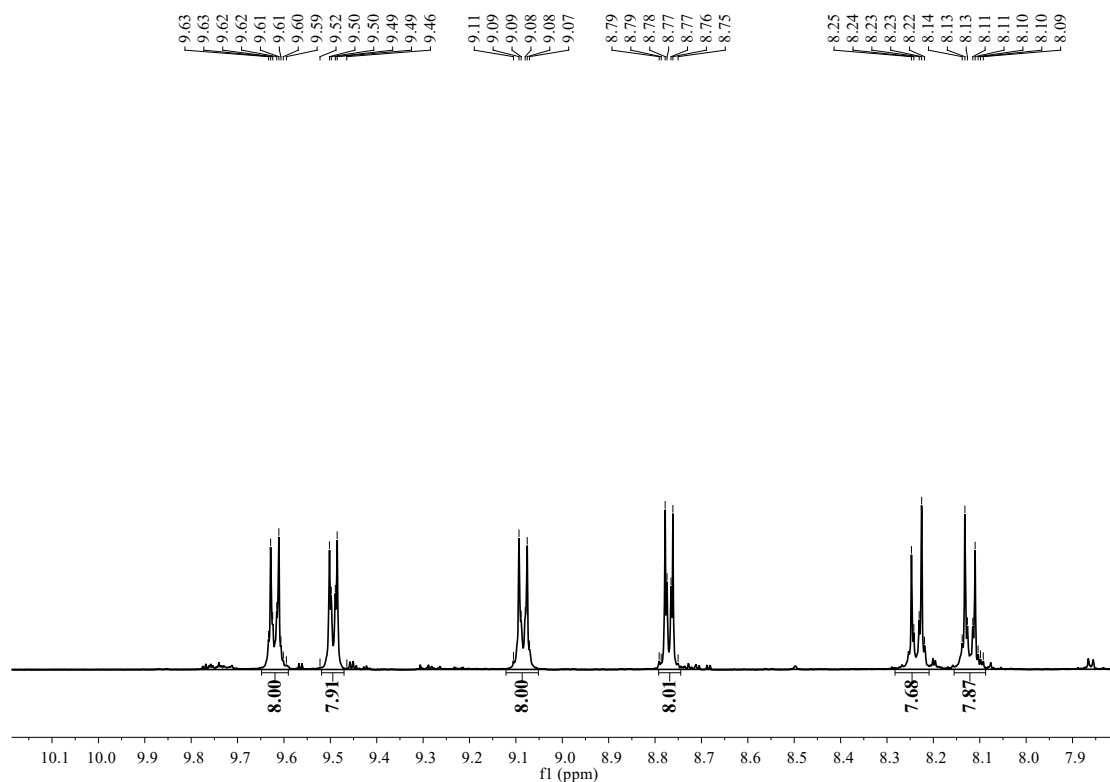
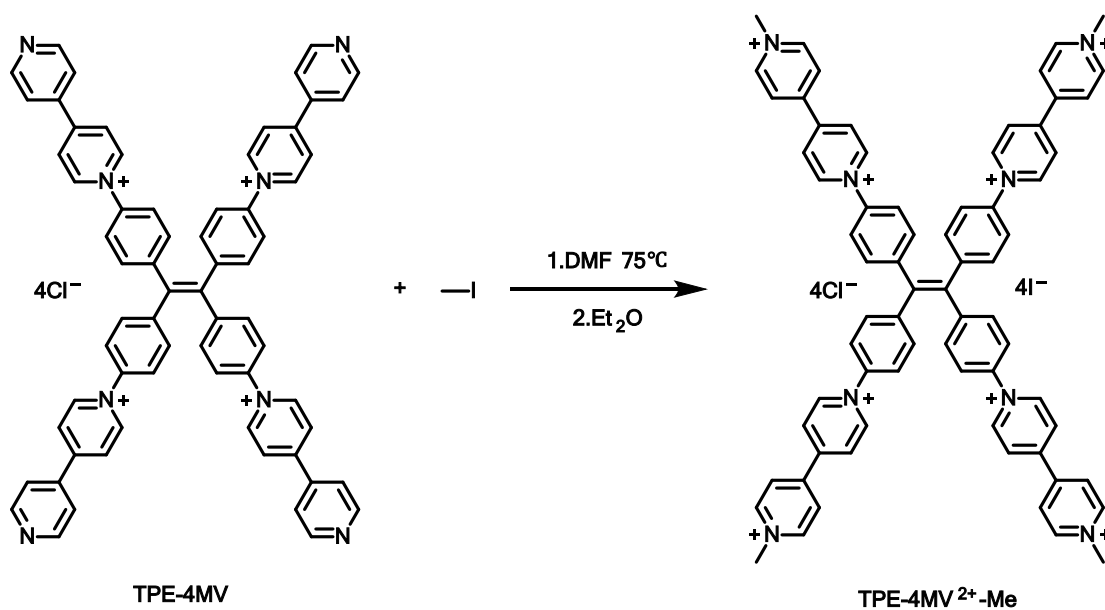


Fig. S2 $^1\text{H-NMR}$ TPE-4MV



Scheme 3 Synthesis of TPE-4MV²⁺-Me

TPE-4MV (1.0 g, 0.92 mmol) and CH_3I (1.3g, 9.2 mmol) were dissolved in N, N-dimethylformamide (DMF), the solution was reacted at 75°C for 24 h. After reaction completed, the mixture was cooled down to room temperature and was slowly dropped

into ether, and the filter cake was collected and dried under vacuum to afford red solid. The corresponding yield was 88%. $^1\text{H-NMR}$ (400 MHz, DMSO-d_6) δ 9.61 (d, 8H), 9.28 (d, 8H), 8.90 (d, 8H), 8.84 (d, 8H), 7.90 (dd, 8H), 7.63 (t, 8H), 4.43 (s, 12H). LC-MS (ESI): m/z $[\text{M-4Cl-4I}]^{8+}$ calculated for $\text{C}_{70}\text{H}_{60}\text{N}_8$: 126.56; found: 126.81.

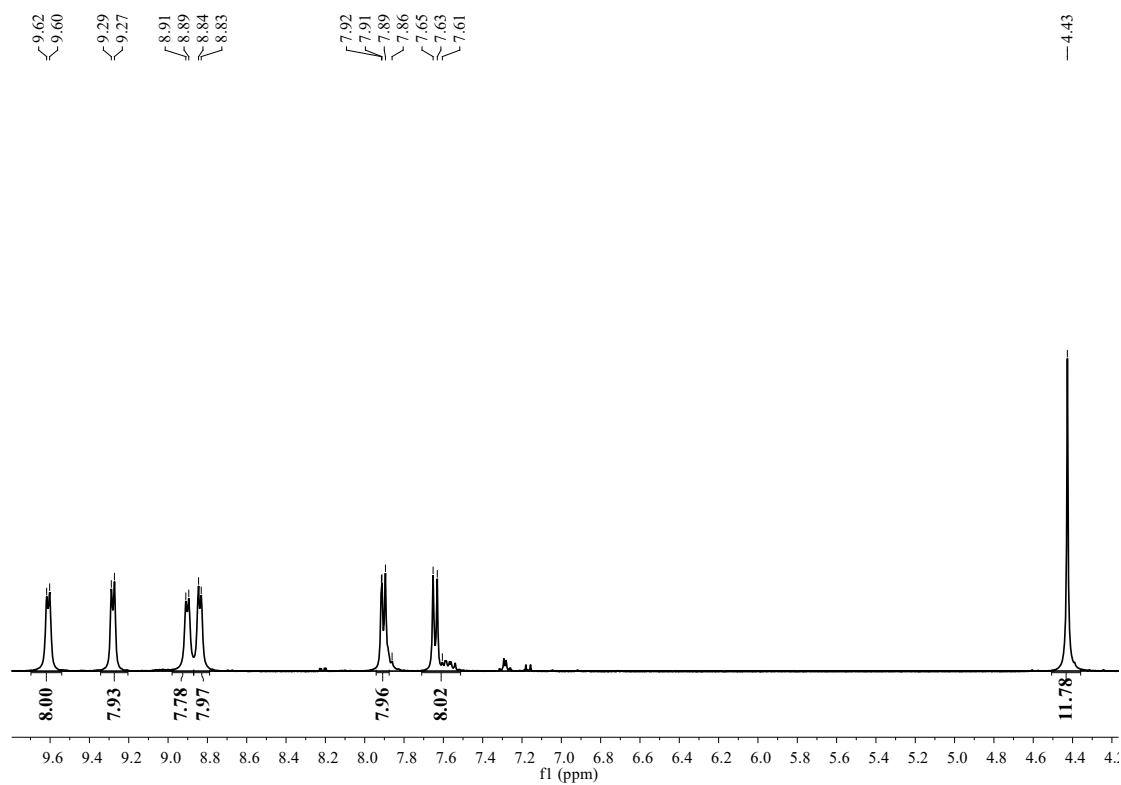


Fig. S3 $^1\text{H-NMR}$ of TPE-4MV $^{2+}$ -Me

4. SDT-induced transient SOFs in the absence of CB[8]

UV-vis and DLS tests were performed to investigate the dissipative performance of TPE-4MV²⁺-Me driven by SDT in the absence of CB[8]. As shown in Figures S4 and S5, the results displayed a similar tendency to TPE-4MV²⁺-Me with CB[8] driven by SDT, indicating that radical-radical interactions lead to the transient self-assembly of TPE-4MV⁺-Me. However, the presence of CB[8] confers longer survival times and larger assembly sizes to transient TPE-4MV⁺-Me. This is attributed to CB[8] significantly enhancing the binding of methyl viologen radical pairs.

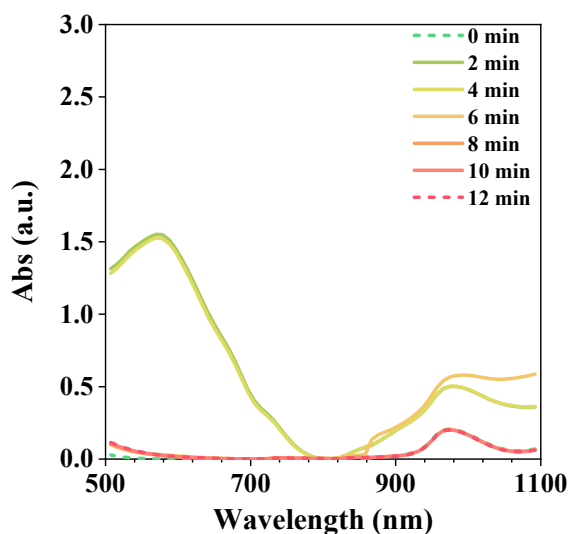


Fig. S4 Time-dependent UV-vis spectra depicting redox behavior of TPE-4MV²⁺-Me triggered by SDT. [TPE-4MV²⁺-Me] = 0.04 mM, [SDT] = 2.4 mM, 25 °C

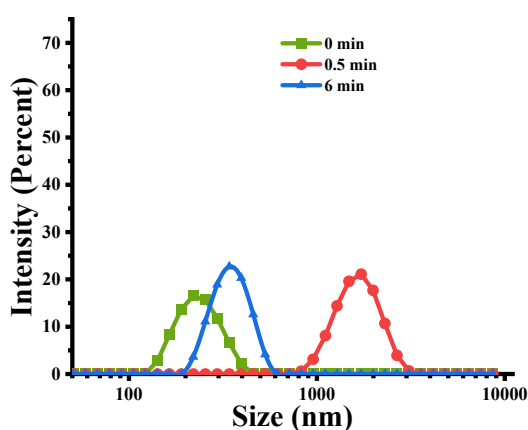


Fig. S5 Time-dependent DLS test depicting redox behavior of TPE-4MV²⁺-Me triggered by SDT. [TPE-4MV²⁺-Me] = 0.04 mM, [SDT] = 2.4 mM, H₂O, 25 °C.

5. Degree of aggregation

To determine the degree of self-assembly by the change of radical-radical interactions. Firstly, we defined the extent of self-assembly of TPE-4MV²⁺-Me/CB[8] as α , according to the change of absorption intensity at 966 nm in Figure 1b, we can obtain the degree of self-assembly by Equation (1)

$$\alpha = \frac{A_{max} - A}{A_{max} - A_0} \quad (1)$$

α ---the degree of aggregation; A_{max} --- maximum absorption intensity at 966 nm;
 A ---absorption intensity at different times at 966 nm; A_0 ---initial absorption intensity at 966 nm.

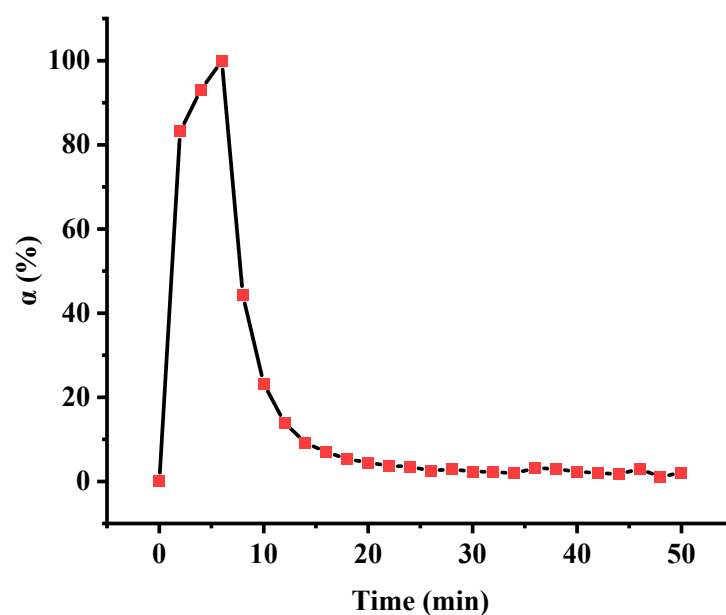


Fig. S6 Time-dependent degree of aggregation depicting redox behavior of TPE-4MV²⁺-Me CB[8] triggered by SDT. [TPE-4MV²⁺-Me] = 0.04 mM, [CB[8]] = 0.08 mM, [SDT] = 2.4 mM, H₂O, 25 °C.

6. DLS test

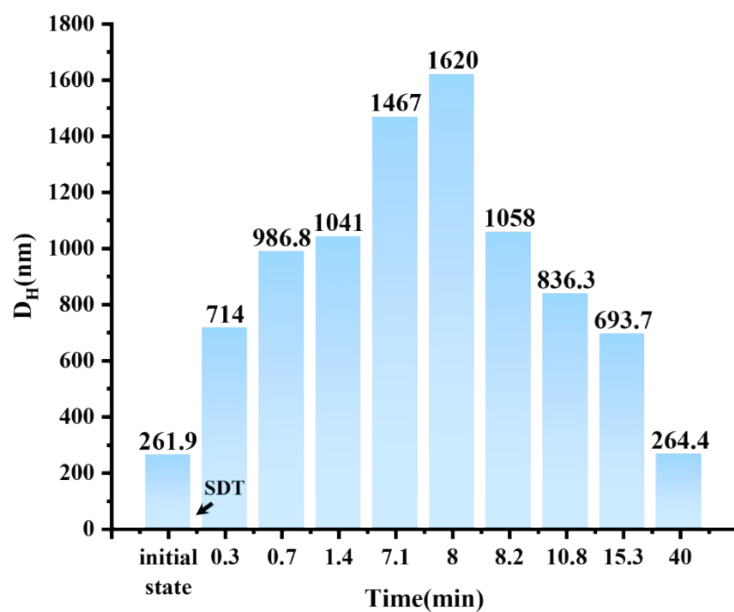


Fig. S7 Time-dependent DLS test depicting redox behavior of TPE-4MV²⁺-Me CB[8] triggered by SDT. [TPE-4MV²⁺-Me] = 0.04 mM, [CB[8]] = 0.08 mM, [SDT] = 2.4 mM, H₂O, 25 °C.

7. SEM images

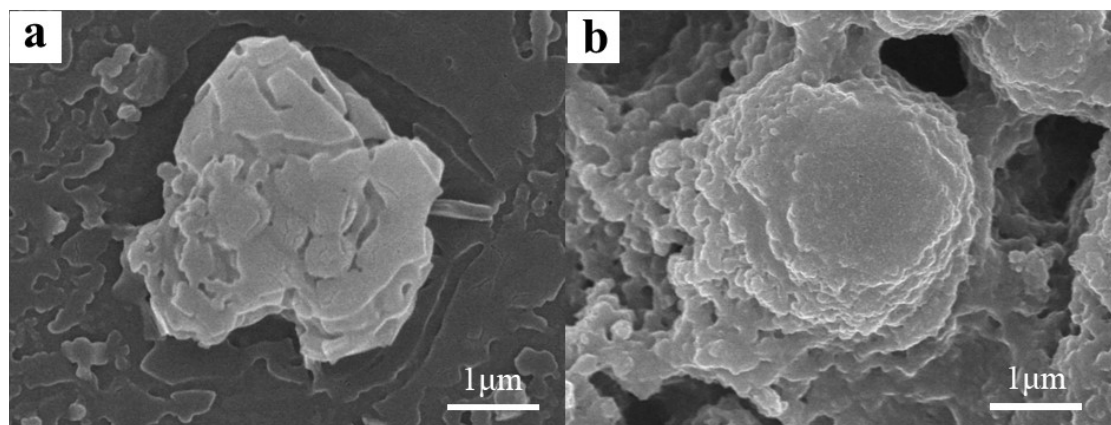


Fig. S8 Magnified SEM image: (a) TPE-4MV²⁺-Me and CB[8]. (b) TPE-4MV²⁺-Me and CB[8] in the presence of SDT. [TPE-4MV²⁺-Me] = 0.04 mM, [CB[8]] = 0.08 mM, [SDT] = 2.4 mM, H₂O, 25 °C.

8. AFM images

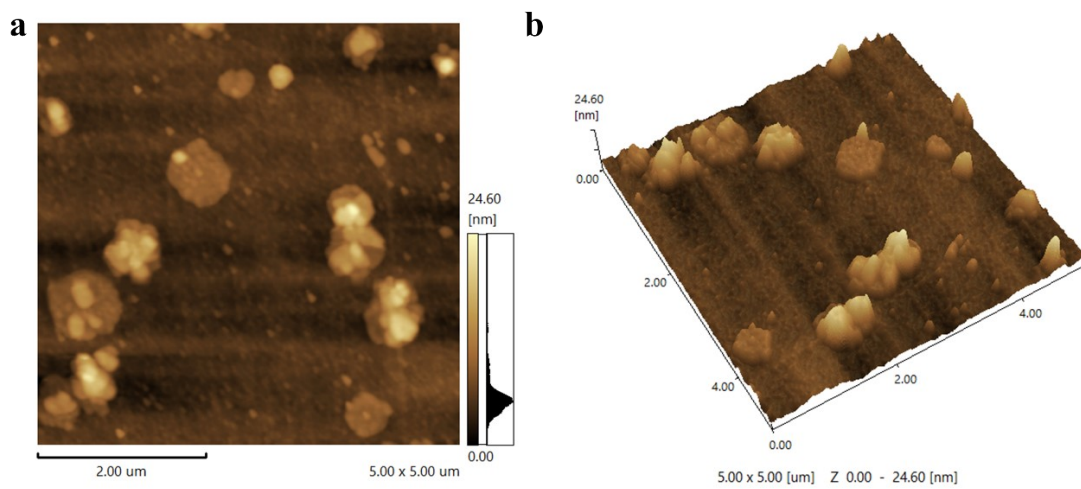


Fig. S9 (a-b) AFM images of TPE-4MV²⁺-Me and CB[8] in the presence of SDT. [TPE-4MV²⁺-Me] = 0.04 mM, [CB[8]] = 0.08 mM, [SDT] = 2.4 mM, H₂O, 25 °C.

9. Coupling of benzyl bromides catalyzed by transient SOFs

9.1 General procedure of synthesis

An oven-dried re-sealable glass penicillin bottle, equipped with a magnetic stir bar, was charged with benzyl bromides (0.02 mmol), TPE-4MV²⁺-Me (0.4-4 μmol), Na₂S₂O₄ (0.04 mmol, 7 mg), K₃PO₄ (0.04 mmol, 8.5 mg), cucurbit[8]uril (0.8-8 μmol), and ultrapure water (2 mL), with nitrogen was filled in the penicillin bottle. The mixture was stirred at room temperature for certain time (2-16 hours). The mixture was diluted in ultrapure water and extracted by chloroform for 3 times. The chloroform solution was dried by decompress distillation and vacuum oven.

9.2 Yield of benzyl sulfones

All the yields were calibrated by Equation (2), and the statistics were obtained for ¹H NMR spectrogram.

$$Yield = \frac{1\alpha}{1\alpha + 2\alpha} * 100\% \quad (\alpha = a, b, c, \dots) \quad (2)$$

where 1α (1a, 1b, 1c, ...) represents the integral value of methylene of benzyl bromides, 2α (2a, 2b, 2c, ...) represents the integral value of methylene of benzyl sulfone. The integral values were normalized.

9.2.1 Model reaction of benzyl bromide

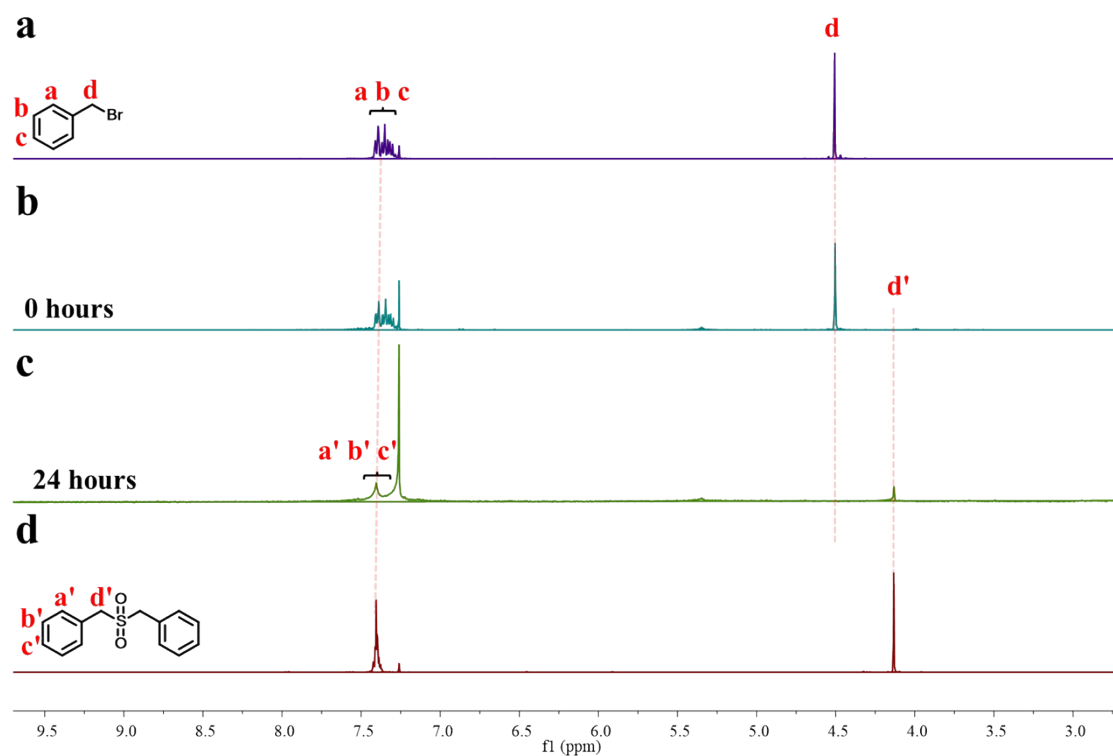


Fig. S10 ¹H-NMR spectra of benzyl bromide (a) and benzyl sulfone (d), ¹H-NMR spectra before (b) and after (c) the transient SOF-catalyzed benzyl bromide coupling reaction. (24h; TPE-4MV²⁺-Me: 4 μmol).

9.2.2 Benzyl bromide catalyzed by TPE-4MV²⁺-Me with varied reaction time

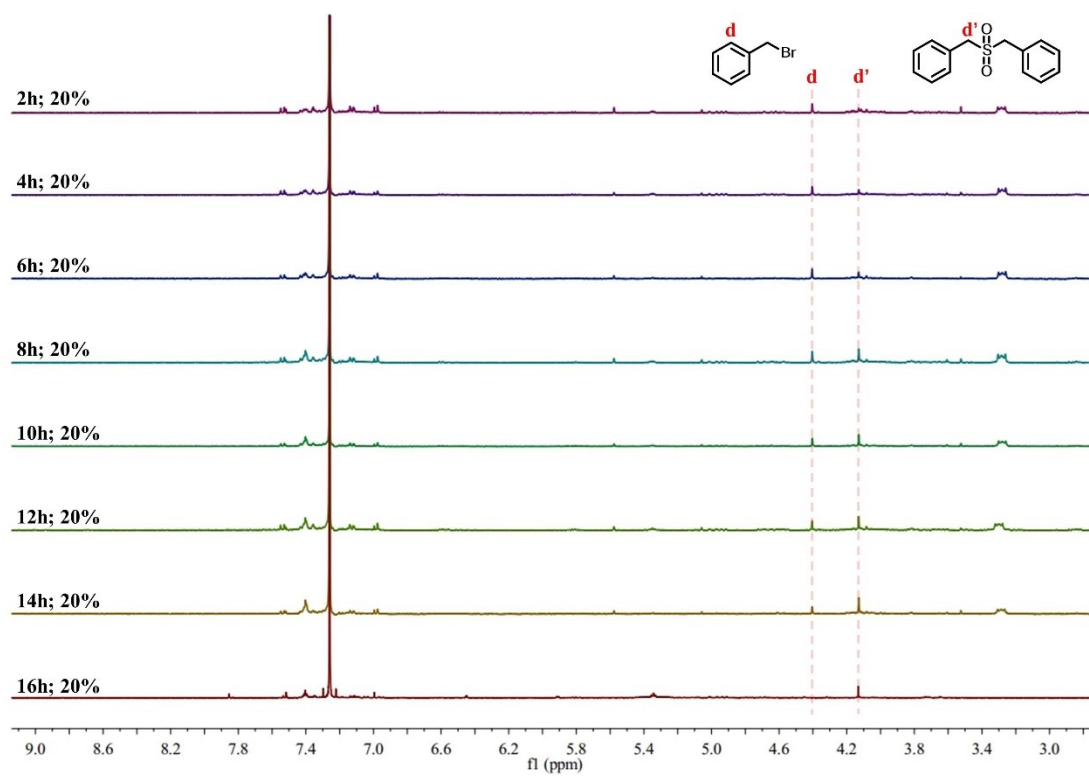


Fig. S11 ¹H-NMR spectra after the transient SOF-catalyzed benzyl bromide (1a) coupling reaction. (Reaction time: 2-16 hours; amount of TPE-4MV²⁺-Me: 4 μmol).

9.2.3 Benzyl bromide catalyzed by varied amount TPE-4MV²⁺-Me

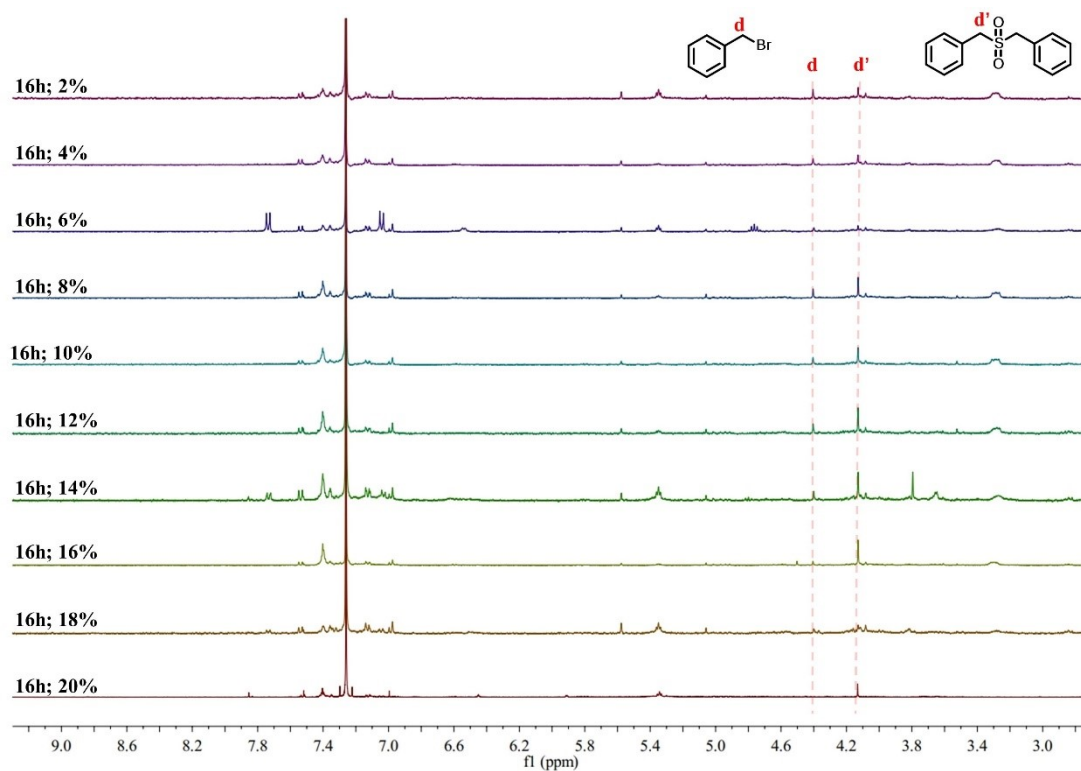


Fig. S12 ¹H-NMR spectra after the transient SOF-catalyzed benzyl bromide (1a) coupling reaction (Reaction time: 16 hours; amount of TPE-4MV²⁺-Me: 0.4-4 μmol).

10. Control experiment of stability of transient SOFs

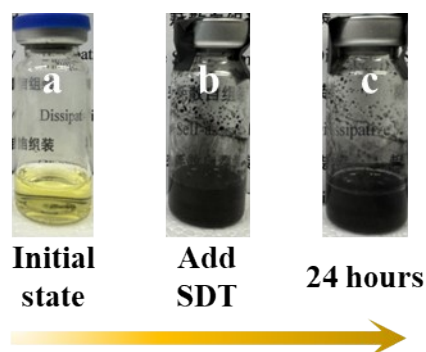


Fig. S13 Time-dependent images of catalysis system in N_2 atmosphere: (a) TPE-4MV²⁺-Me, CB[8] and K₃PO₄; (b) TPE-4MV²⁺-Me, CB[8] and K₃PO₄ after adding SDT; (c) TPE-4MV²⁺-Me, CB[8], K₃PO₄ and SDT in N_2 atmosphere for 24 hours. [TPE-4MV²⁺-Me] = 0.04 mM, [CB[8]] = 0.08 mM, [K₃PO₄] = 0.02 mM, [SDT] = 2.4 mM, H₂O, 25 °C.

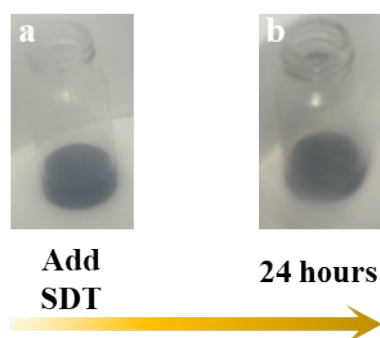


Fig. S14 Time-dependent images transient SOFs in vacuum atmosphere: (a) TPE-4MV²⁺-Me, CB[8] and SDT in N_2 atmosphere; (b) TPE-4MV²⁺-Me, CB[8] and SDT in N_2 atmosphere for 24 hours. [TPE-4MV²⁺-Me] = 0.04 mM, [CB[8]] = 0.08 mM, [SDT] = 2.4 mM, H₂O, 25 °C.

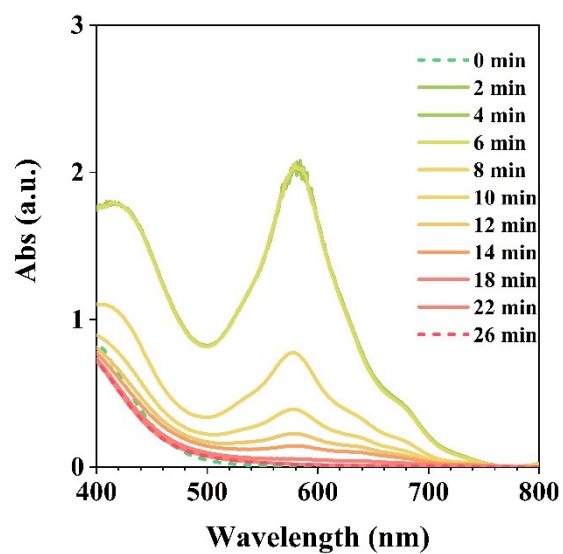


Fig. S15 Time-dependent UV-vis spectra depicting redox behavior of TPE-4MV²⁺-Me triggered by SDT, TPE-4MV²⁺-Me solution was pumped into N₂ for 10 minutes before adding SDT. [TPE-4MV²⁺-Me] = 0.04 mM, [SDT] = 2.4 mM, 25°C

11. Notes and references

1. Y. Wang, N. Han, C.-Q. Ma, H. Liu, S. Yu, R. Wang, V. K. Thakur and L.-B. Xing, *Nano Materials Science*, 2023, **5**, 335-342.